Fouling and cleaning synergy in ultrafiltration membrane systems -- chemical cleaning after filtration of spent sulphite liquor

Weis, Andreas

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Fouling and Cleaning synergy in ultrafiltration membrane systems

Chemical cleaning after filtration of spent sulphite liquor

Submitted by Andreas Weis

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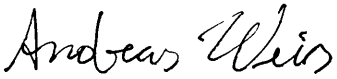

Andreas Weis

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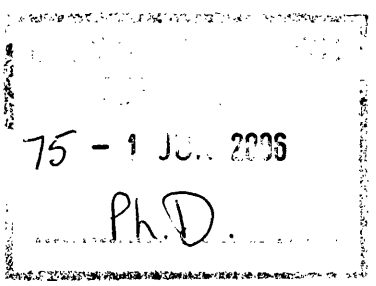
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Summary

Fouling of membranes is well understood, and is the major factor responsible for the long-term decline of permeate flux during membrane separation. When chemical cleaning is carried out, the flux decline can be minimised or eliminated. However, the interrelationship between fouling and cleaning over many operational cycles is not well understood, and was the central phenomenon investigated during this project.

To study this process, a flat sheet membrane module and a rig was designed. Spent sulphite liquor was used for experimentation, owing to its industrial significance.

Whilst permeate flux is an important parameter in characterising membrane performance, it is a poor indicator of surface conditions. Therefore in addition to filtration data such as flux and retention, the hydrophobicity, charge and surface morphology of polyethersuphone (PES), polysulphone (PSf) and regenerated cellulose (RC) membranes were investigated. Atomic force microscopy pictures were taken in order to obtain information concerning the surface properties of used membranes. At different stages of the fouling and cleaning process the fouling material, its charge and hydrophobicity were characterised using ATR-FTIR, extraction, zeta-potential and contact angle measurements. For short and long term fouled membranes the concentration and temperature optima for the cleaning step were investigated.

The results demonstrate a strong relationship between the membrane filtration performance and the surface properties of the used membranes, the membrane material, the foulants and the cleaning agents.

Over multiple operational cycles, when cleaned with NaOH the PES membrane showed a flux decline of only 45%, compared to a corresponding value of 85% for the PSf membrane. When cleaning with Ultrasil 11 the difference in flux decline values for the two membranes was even higher. The differences in porosity and total area between the two membranes resulted in a strong absorbance of surfactants for the PES membrane and maintained the flux above the value for the virgin membrane, whereas the flux for PSf dropped by 50% when using *Ultrasil 11*. For the very hydrophilic RC membrane the fouling

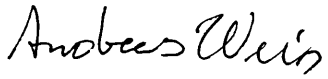
tendency was low in comparison to that seen for the PES or PSf membranes. The limited surfactant adsorption to the RC membrane resulted in a smooth flux decline over long term, resulting in a 50% reduction in flux when using either NaOH or Ultrasil 11 cleaning agents over multiple operational cycles.

Over the short term the membrane material, its porosity, and surface roughness are the dominant factors in determining the cleaning performance. Over the longer term, the surface becomes irreversibly fouled, and physico-chemical interactions between the cleaning agent and foulant are dominant, and the influence of the membrane material itself becomes less significant.

Acknowledgements

I owe an enormous dept to some colleagues, friends and co-workers over the last years as we attempted to learn and understand the basic principles of membrane separation and interfacial phenomena, such as surface chemistry and physics. I would like to name here especially Arto Pihlajamäki, Hwee Chuan Chua and May Ling Yeow and thank for the discussions and help. Although, because of the nature of research, the study was often the blind leading the blind, with many hesitations and frustrations, the exercise was always challenging, stimulating and generally productive.

I wish to thank and to dedicate this thesis to Dr. Michael R. Bird and Prof. Marianne Nyström, both pioneering membrane separation and cleaning of membranes and supporter, promoter, and encourager of often inexperienced people with new and interesting ideas. Last but not least I would like to thank my parents for the moral support and Jun Lucy Luo for always finding the right words in any situation.



Andreas Weis, Lappeenranta, January 2004

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Nomenclature

ABBREVIATION	DESCRIPTION
AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total reflection Fourier transform Infrared spectroscopy
BTU	British Thermal Units
$CaCO_3$	Calcium Carbonate
$CaSO_4$	Calcium Sulphate
CFV	Cross Flow velocity
CP	Concentration Polarisation
DF	Diafiltration
EDL	Electric double layer
EDTA	Ethylene diamine tetraacetic acid
FI	Flow meter display
HCL	Hydrochloric acid
HMM	High molecular mass fraction
IR	Infrared
kD	Kilo Dalton
LMM	Low molecular mass fraction
LS	Lignosulphonate
LUT	Lappeenranta University of Technology
MF	Microfiltration
MMCO	Molecular mass cut off
NaOH	Sodium Hydroxide
NF	Nanofiltration
PWF	Pure water Flux
PF	Product Flux
PES	Polyethersulphone
PIT	Pressure transducer
PSf	Polysulphone
PSU	Possible structural units
QIT	Conductance transducer

QI	Display potential
RC	Regenerated Cellulose
Re	Reynolds Number
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SSL	Spent sulphite liquor
UF	Ultrafiltration
TTT	Temperature transducer
TMP	Transmembrane pressure
U	Electrical current
UV	Ultraviolet
VHV-S	Company code for SSL liquor made from softwood (Norwegian spruce)
VS-850	Company code for SSL liquor made from a mixture of soft- and hard wood.

SYMBOL	DESCRIPTION	UNITS
a	Height	m
b	Width	m
c	Concentration	$g\ L^{-1}$
c_m	Concentration at membrane surface	$g\ L^{-1}$
c_p	Concentration in permeate	$g\ L^{-1}$
c_b	Concentration in feed(bulk solution)	$g\ L^{-1}$
c_g	Gel layer concentration	$g\ L^{-1}$
c_f	Concentration in feed	$g\ L^{-1}$
ΔC	Concentration Difference	$g\ l^{-1}$
^oC	Degree Centigrade	-
d	Diameter of a circular channel	m
d_e	Diameter of a rectangular channel	m
d_p	Depth of penetration	cm
D	Diffusion constant	$m^2\ s^{-1}$
E	Electrochemical Potential	V

ΔE	Electrochemical Potential Difference	V
F	fouling	
J	Mass flux	kg m^{-2} h^{-1}
J_n	Flux at n cycles	kg m^{-2} h^{-1}
J_o	Flux of the virgin membrane	kg m^{-2} h^{-1}
k	Mass transfer coefficient	m s^{-1}
k_s	Mass transfer coefficient for solute	m s^{-1}
l	Length of channel	m
l_n	number of channels	-
n	number of fouling and cleaning cycles	-
n_1	Refractive index of crystal	-
n_2	Refractive index of sample	-
p	Pressure	bar ($10^5 Nm^{-2}$)
ΔP	Transmembrane pressure	bar ($10^5 Nm^{-2}$)
p	Pore blocking	-
ppm	Parts per million	-
q		
Q	Volumetric flowrate	m^3 s^{-1}
R	pore size	m
R	Resistance	m^{-1}
R_a	Adsorption resistance	m^{-1}
R_g	Gel layer resistance	m^{-1}
R_m	Membrane resistance	m^{-1}
R_p	Pore blocking resistance	m^{-1}
R_{cp}	concentration polarisation resistance	m^{-1}
t	time	s
T	Temperature	°C
ΔT	Temperature Difference	°C
u	average linear velocity	m s^{-1}
V	Volume	m^3
wt	weight	kg
W	Wavenumber	cm^{-1}
x	normal distance from membrane	

GREEK

α	Angle of incidence	^{o}
δ	Boundary layer thickness	m
Δ	Difference	-
ε_o	Permittivity of a vacuum	$F\ m^{-1}$
ε_r	Relative dieelectric constant of the electrolyte	-
ζ	Zeta-potential	V
η	Kinematic Viscosity	m^2s^{-1}
κ	Conductivity of the electrolyte solution	$1\ m^{-1}$
θ	Contact angle	-
λ	Wavelength	cm
μ	Dynamic Viscosity	$kgm^{-1}s^{-1}$
π	pi	3.1427
ρ	Density	kgm^{-3}

Chapter 1

Introduction

1 Introduction

Separation processes with porous membranes, such as Micro- (MF), Ultra- (UF) and Nanofiltration (NF) are well established in all kinds of industry, since they show substantial economical and environmental benefits compared to traditional separation methods. New industries who are faced with the decision making process of investing in new equipment or old established industries that need to replace old installations, often decide to switch to membrane technology. The latest available figures show staggering numbers of annual sales for membranes and modules. In Table 1.1 a range of membrane processes are presented. It should be pointed out that despite the fact that MF and UF are among the oldest methods for membrane separation, they continue to grow exponentially, *Bennett* 2002 (see Figure 1.1).

Unfortunately a major drawback and continuing problem in membrane applications is the adsorption of material at the membrane. This can cause a reduction in flux and separation performance up to a degree where membrane technology is not competitive with other separation methods. Therefore, along with the development of membranes a great amount of research is on the way to overcome the fouling problem. For example, the development of new modules with improved fluid dynamics, or physical cleaning procedures and cleaning agents. Doing research on fouling of membranes, one should be aware of the fact that fouling tendencies depend upon the solutes which have to be separated, which makes it difficult to generalise findings and apply them to other membrane separation tasks. Therefore, the two steps, fouling and cleaning remain an empirical science, where the membrane manufacturer has to rely on experience to offer customers standardised cleaning procedures for their processes. Nevertheless, continuing efforts in this particular field of membrane research have lead to new analytical methods, which make it possible to monitor the fouling process and track down the solutes which cause the onset. Furthermore with these new tools a more scientific approach to the fouling and cleaning problem can be expected.

Table 1.1: Worldwide sales of membranes and modules for various membrane processes (adapted from Strathmann 1999)

Membrane process	Sales in 1998, in million $	Growth, % p.a.
Dialysis	1900	10
Microfiltration	900	8
Ultrafiltration	500	10
Reverse Osmosis	400	10
Gas exchange	250	2
Gas separation	230	15
Electrodialysis	110	5
Electrolysis	70	5
Pervaporation	>10	/
Miscellaneous	30	10
Total	4400	>8

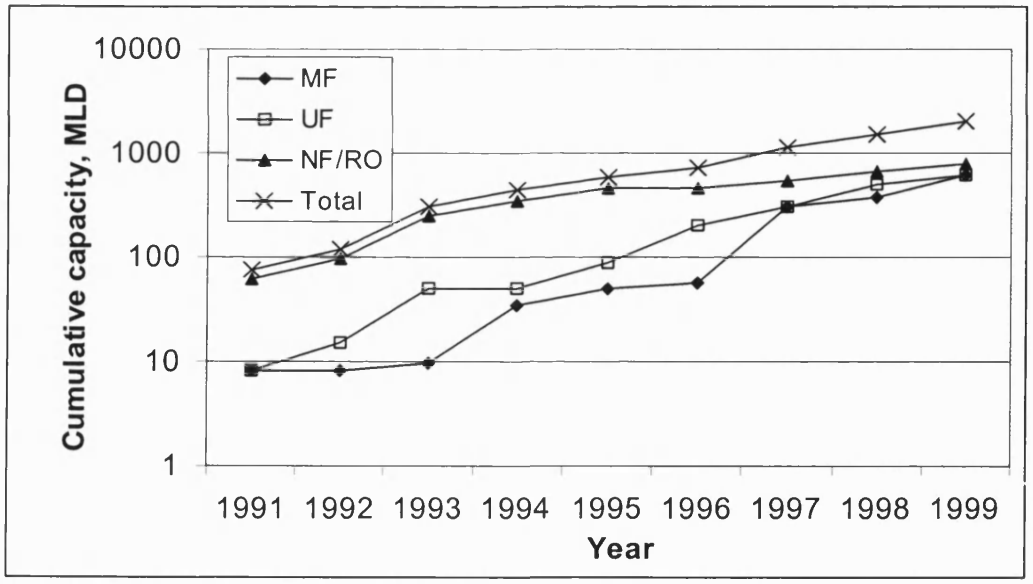


Figure 1.1: Membrane capacity growth, redrawn from Bennett 2002 (data from Vivendi water). MLD=Million liter daily.

1.1 Why cleaning ?

Basically the drop in separation performance of membranes can be seen from two viewpoints. First, one can argue the drop is due to fouling or one could also say it is because of insufficient cleaning. In the past this question was not even asked in this way, since no or little knowledge at all was available about both sides of the problem. Naturally, most research so far reported was focusing on the fouling behaviour of all kinds of materials, since it is logical to investigate first the causes of fouling, rather than removal. A literature review on fouling investigations in the past can be found in *Espig* 1997 and *Bartlett* 1998. The common idea is that for the removal of fouling, knowledge of the fouling layer composition and build-up is necessary. But with the knowledge of fouling increasing, the interest in cleaning started to rise. *Doulia et al* 1997 pointed out the possible strong relationship between fouling and cleaning and hence the consequences for the long-term performance. *Dal-Cin et al* 1996 and *Rabiller-Baudry et al.* 2002 emphasised in general that long term tests are needed to study fouling and cleaning. The hypothesis was raised that cleaning has over long term an even more deteriorating effect than the fouling, due to for instance interaction with the membrane polymer, (*Gan et* al. 1999 and *Wallberg et al.* 2001). *Muñoz-Aguado et al.* 1996 assumes that control of the surface-chemistry will determine subsequent fouling behaviour. Both directions, fouling and cleaning research have lead to new analytical tools (*Bowen* 1984 and *Nyström* 1994) and improved cleaning procedures (*Shorrock and Bird* 1998). In the literature the fouling problem is often related to separation tasks in industries, where complex substances have to be separated, rather than for other industries, where just two different substances are involved.

1.2 Concepts and Definitions [Adapted from Bartlett 1998]

The cleaning process involves the removal of extraneous materials from the system with the aim of restoring the surface to a pristine condition.

Cleaning is required to overcome the soil/membrane and soil/soil adhesion forces. The necessary energy required for deposit removal can be supplied by chemical cleaning agents which react with the deposit and modify the interface, or kinetic energy provided in the form of solution velocity and /or deposit shear stress. Thermal energy improves the reaction and hydraulic dynamics (*Espig* 1997). The energy to remove soil is usually supplied as a combination of all three. Compatible chemicals are used to remove the deposit in a cross-flow system at elevated temperatures.

Generally, cleaning procedures applied to fouled membrane systems consist of a series of rinsing and cleaning cycles followed by a sanitation step. It is important to distinguish between the different procedures involved in the cleaning process.

When only water is used to remove deposited material the operation is called rinsing and any cleaning is by the mechanical action and solvating power of water. The mechanisms of rinsing have been extensively reviewed by *Nakanishi et al.* 1985, *Plett* 1985 and *Kulozik et al.* 1989.

If a chemical agent is used the process is called cleaning or disinfection. Disinfection (or sanitation) is only concerned with the destruction of pathogenic micro-organisms and the reduction of organisms which degrade the product, *Luss* 1984, whereas cleaning entails the removal of all extraneous material. Thus, it is implied that a clean surface should be free of any kind of soil. The degree of cleanliness required varies substantially from industry to industry. *Romney* 1990 summarised the three target levels of cleanliness as:

- **Physically clean** – free from visible impurities
- **Chemically clean** – free from chemical impurities
- **Biologically clean** – free from living micro-organisms

The physical state of the membrane can be assessed by visual inspection. Physical action can be used to remove any gross deposits that are detected. It is not usually possible to remove strongly attached or adsorbed material from the surface or pores of the membrane by these physical means alone.

The removal of strongly attached material is possible through a combination of chemical and physical cleaning methods. Residual fouling or cleaning contamination affects the subsequent membrane performance, but is undetectable by visual examination. The adsorption of foulants and cleaning agents can cause irreversible changes to the membrane surface. This suggests that a used membrane can never be cleaned to its original pristine condition.

The aim of the membrane cleaning process is to restore permeability and retention to the same level as found with a virgin membrane. However, the industrial reality is of a system where it is considered sufficient to clean the membrane such that its subsequent behaviour is standardised.

1.3 The economic aspect of cleaning

Cleaning becomes necessary if a replacement of membranes is more expensive than the inconvenience of the cleaning procedure, since cleaning itself causes supplementary costs (*Bartlett* 1998) like,

- Loss of production
- Product loss
- Labour costs
- Energy costs
- Costs for cleaning agents
- Effluent treatment (environmental impact)

Blackwell et al. 1992 estimated that the costs for the cleaning agent itself to clean a UF plant used for processing pulp and paper effluent is the highest among all other operating costs listed above. His calculations are based on an average of 2.5 times cleaning every week for two hours and a detergent cost of 4 US $/kg. *Maples and Lang* 1979 reported similar frequencies of washing.

1.4 Scope and aims of the study

In the past intensive research has been taking place on:

- mechanism of fouling and development of biofilms
- tools to characterise fouling mechanisms and biofilms
- mechanical cleaning methods
- chemical cleaning agents
- chemical cleaning protocols

Within the published results of these research fields growing evidence can be found, that there is a relationship between deposition and cleaning cycles. It is reported for example, that after fouling and cleaning cycles, UF membranes show the same separation performance as new membranes with different molecular mass cut off's (MMCO), *Dal-Cin and co-workers* 1996 and *Gorenflo* 2000. *Kim et al. 1993* have already pointed out that cleaning performance will depend on the electrostatic interaction between the fouling layer and the cleaner and assumes that it will have a profound effect on membrane lifetime. Other researchers do not specially target cleaning. They look at solution chemistry and have found that in particular the interaction of surface charges between membrane, foulant in solution and already adsorbed foulant will influence further adsorption of foulants, *Li and Fu* 2002. Besides the surface chemistry *Li and Fu* as well as *Hong and Elimelech* 1997 report that the transmembrane pressure has a synergetic effect, either enhancing or decreasing it, depending on the solution chemistry. It is also reported that the fouling material is separated into different layers, composing different chemical substances. This raises the question, whether the choice of cleaner should be changed by approaching the phase where

a second different fouling layer is built up or the fouling layer is modified by the cleaning agent used in the initial stages. Another reported problem is the hardening of the foulants, which describes the phenomena that some deposits are more difficult to remove after ageing *Gillham et al.* 1999. The ageing problem of the foulant material itself raises the question, if a cleaning protocol, which is less successful for short term, might be perhaps better for long term cleaning results.

There is clear evidence that there is interaction between the membrane, soil and cleaner, *Lindau* 1995. In this study the objective is not so much to show further evidence for this, but to investigate how significant these synergetic relationships are and how they affect the efficiency of the process.

With this project an attempt is made to answer some fundamental questions:

1. *What is the synergistic effect between fouling and cleaning processes?*

Is the interaction between fouling and cleaning based more on chemical interactions between membrane material, fouling material and cleaning agents or will it be determined by physical effects, such as pore plugging, surface fouling or compaction?

2. *When does the long-term performance of a membrane start?*

In the past fouling and cleaning results with a small number of cycles were published. The focus was on evaluating fouling mechanisms, and it was only necessary to foul the membrane once. But how will the membrane perform after many fouling and cleaning cycles? And how will negative or positive synergistic effects have an influence on subsequent cycles or in other words, long term performance?

3. *How can the change in performance be detected?*

Direct tools are retention and flux measurement. But indirect tools, like zeta-potential measurements, attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) and atomic force microscopy (AFM) or scanning electron microscopy (SEM) pictures should also be considered.

4. How can the difference between short and long term performance be defined?

A considerable definition of long term performance could be for example the reaching of a performance equilibrium, which means where no change of performance occurs between fouling and cleaning cycles.

1.4.1 Choice of the feed solution

One should be aware that the feed solution is an important factor by answering scientific questions concerning fouling and cleaning. The use of a certain feed solution makes the membrane system unique and a direct transfer of results to other membrane systems makes it therefore questionable. But even though the chemical reaction mechanisms for the fouling is different, the physical results are the same and lead to common fouling problems, like internal and external fouling, or adsorption. Also, the goal is to gain fundamental new knowledge, and the major task is to prove the existence of phenomena described above.

Therefore, the feed solution was selected carefully, in order to cause common fouling problems: the selected fouling material has

- Good fouling potential
- Multiple composition of different potential foulants
- Foulants have different molecular sizes and charges
- Mirrors an actual industrial fouling and cleaning problem
- Easy and cheap to obtain
- Easy to store, with no microbiological growth occurring

A foulant with these criteria was found in spent sulphite liquor, with the major ingredient, the lignosulphonate (LS).

1.5 Thesis organisation

Following this brief introduction this thesis is divided into 5 subsequent chapter as well as references and appendix.

Chapter 2 details the process and design considerations required for membrane testing over multiple operational cycles for spent sulphite liquor and special considerations for the pulp and paper industry

Chapter 3 describes the experimental system developed and classifies the materials and methods used.

Chapter 4 describes the analytical results obtained through extensive experimental study and discusses them with reference to the relevant literature.

Chapter 5 describes the filtration results obtained through extensive experimental study and discusses them with reference to the relevant literature.

Chapter 6 summarises the results and draws conclusion. From those conclusions recommendations and proposals for future work are given.

Chapter 2

Process

and

Design

Considerations

2 Introduction

With the widespread application of membrane separation technologies in all industrial sectors, the fouling problems became ever more a problem for the implementation of this technology. The costs of a process are the key for the introduction of a new technology, such as membranes. Therefore, in industries with high revenues per manufactured item, the fouling phenomena can be accepted. The lower the revenues become per manufactured unit, the higher the obstacle for the introduction of membrane technology becomes. Such industry with high output and low revenue is regarded as a bulk industry. Examples can be found in the chemical and food industry or the pulp and paper industry. The need for overcoming the fouling problem is further enhanced by legislation, such as the build up of closed water recycling systems, *Nuortila-Jokinen* 2002.

Therefore for the experimental work of this study, a process was chosen, that belongs to this group of bulk industries, and has not previously been well investigated.

The membrane fractionation process of lignosulphonates was chosen where the aim is to separate and concentrate different molar mass fractions. The feed material comes from the sulphite pulping process, and is a by-product of the paper making process. A brief outline of the pulping process is described below.

2.1 The processing of wood pulp [According to Gullichsen and Fogelholm, 1999]

Since it is important to know something about the base material for the later analyses of results and for discussion, a short description about the main aspects of wood pulp processing related to the fouling and cleaning problem will be given:

The paper industry needs cellulose fibres as a base material to produce paper. The first stage in this process is the grinding of trunks to gain wood chips. These chips are then cooked under pressure, high temperatures and acid conditions. The aim is to extract the lignin between the cell walls and bring it into the water-soluble form. This can be done with the „Kraft"-pulping process, which leads to the Kraft-Lignin or the sulphite pulping process, which leads to the lignosulphonates. Both ways delivering different kinds of water-soluble lignins, but if the aim is to use the lignins for further processing, then the lignosulphonate's are still the preferred ones.

After the cooking the cellulose can be easily removed by sedimentation and the remaining liquor can then be fermented to make use of the monosaccharides and ultrafiltered to recover the lignosulphonates. The LS are just a by-product of the paper making process, but have found a vast amount of application in the food and chemical industry as binders and adhesives. The most popular example from the food industry area is the usage of high molar mass lignosulphonate as precursor for the production of Vanillin, see also Figure 2.1 below.

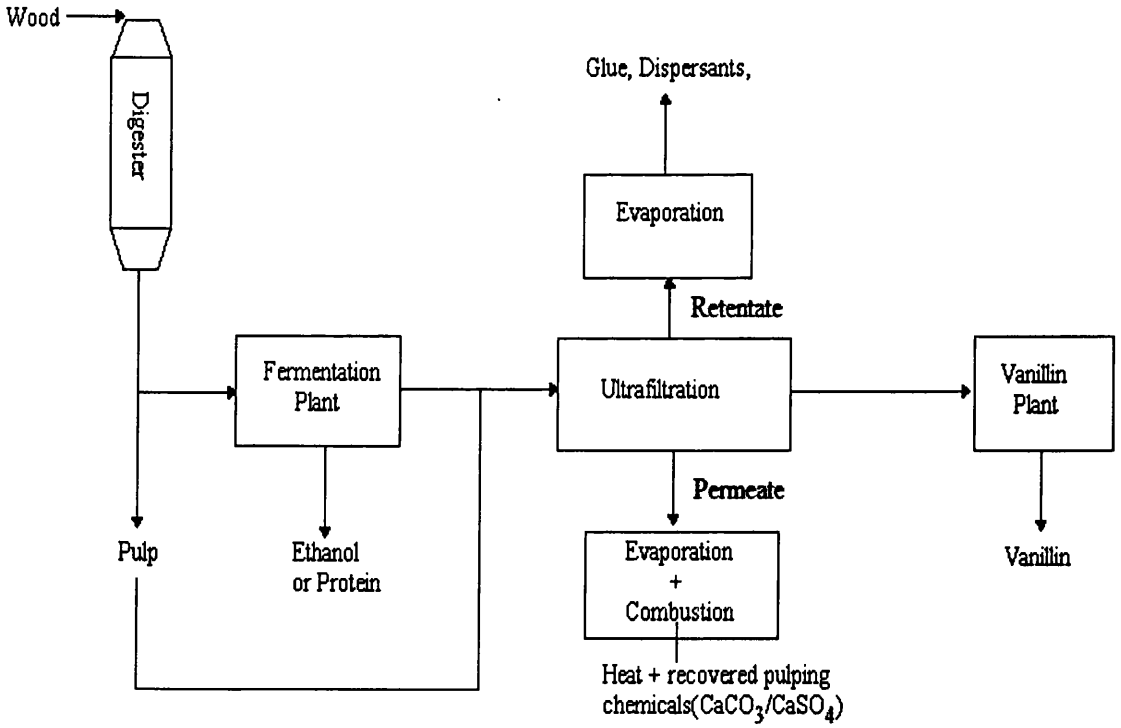


Figure 2.1: Processing of wood pulp

2.2 Membrane Separation Processes

2.2.1 Basic Principles [According tor Mulder 1996]

Generally in membrane based separation processes a liquid or gaseous mixture of different components is divided into feed and permeate. The feed is the solution entering the membrane module or process and permeate is the solution which has passed through the membrane. During this separation at least one component of the mixture is rejected and remains in the feed stream (see Figure 2.2).

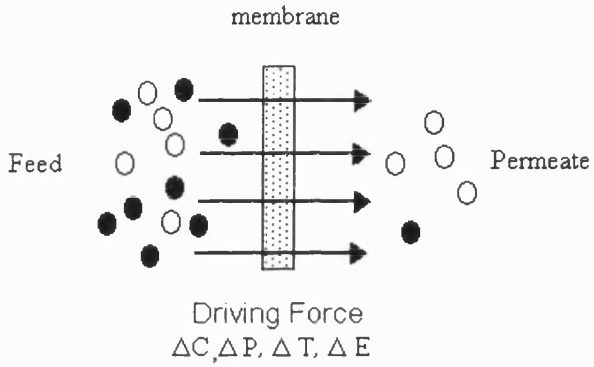


Figure 2.2: Schematic illustration of the membrane separation principle (after Mulder, 1996)

For membrane processes, three separation mechanisms can be distinguished briefly (see Figure 2.3).

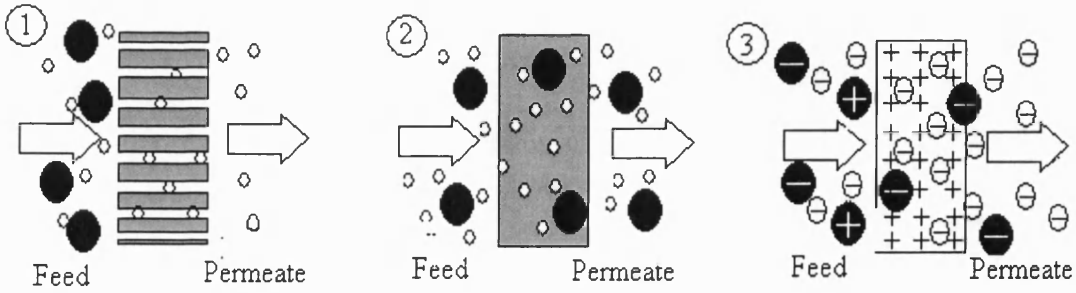


Figure 2.3: Membrane separation mechanisms: (1) sieving mechanism, (2) solution-diffusion mechanism,(3) and ion exchange mechanism.

The sieving mechanism is used to describe the mass transport through porous membranes. The separation is based on the pore diameter. That means only particles with a diameter lower than the pore diameter can pass through the membrane. Therefore an enrichment of the smaller particles, or molecules takes place in the permeate, (see Table 2.1 for the differentiation of the four pressure driven membrane processes).

The solution-diffusion mechanism is typical of dense membranes. Here, the separation is based upon the solubility of a component in the membrane material and its diffusion through the membrane. This mechanism can therefore be used for the separation of molecules. Due to solution-diffusion, the quality of the process is mainly determined by the affinity of the membrane material to the molecules, that ought to be separated. The solution-diffusion mechanism is the separation mechanism of pervaporation. Due to the affinity of pervaporation membranes to polar and nonpolar molecules, the pervaporation process distinguishes between hydrophilic and hydrophobic pervaporation. The third mechanism is based upon charges in the membrane. The fixed charges cause a rejection of ions with the same charge. This mechanism is used in electrodialysis and partly in nanofiltration.

Table 2.1: Pressure driven liquid phase membrane process, (Fane 2001). no pores detectable by electron microscopy.*

PROCESS	PRESSURE-RANGE	PORE SIZE	REMOVED	PERMEATING [WATER+SPECIES]
RO	10-20 bar	*	most solutes	(some) small ions
NF	5-10 bar	0.5-2 nm	multivalent ions, organics	(some) monovalent ions, Low molecular mass organics
UF	1-5 bar	2-100 nm	colloids, macrosultes	Ions, organics
MF	0.1-1 bar	0.1 - 1μm	colloids, particles(>0.1 mm)	other species

2.3 Advantages of membrane technology in the pulp and paper industry

The use of membranes in the pulp and paper industry can be divided into three main fields:

- Use for separation of valuable chemicals from effluent streams
- Pollution control and waste management
- Resource saving (Energy, Water)

For spent liquors (Sulphite, Kraft) following membrane techniques are in use. The traditional technique was evaporating the effluent after the liquor has left the digester. By applying ultrafiltration ahead of the evaporator, 50 to 75% of the water can be removed at a much lower energy cost than by simple evaporation alone. During the ultrafiltration the effluent can be fractionated and concentrated in higher molar mass lignosulphonates in the retentate and the low molar mass lignosulphonates in the permeate stream. Since the later still contains too many solids (4-6%) it can neither be discharged into a river, nor economically evaporated for disposal from such low concentrations. Therefore, a reverse osmosis system is added to remove these solids down to 0.1% and it is then clean enough for discharge into a river. The retentate together with the UF concentrate is recycled to the evaporator. A complete flow diagram of the UF and RO separation system can be seen in Figure 2.4 and energy use comparison of different techniques in Table 2.2, *Paulson and Spatz* 1983.

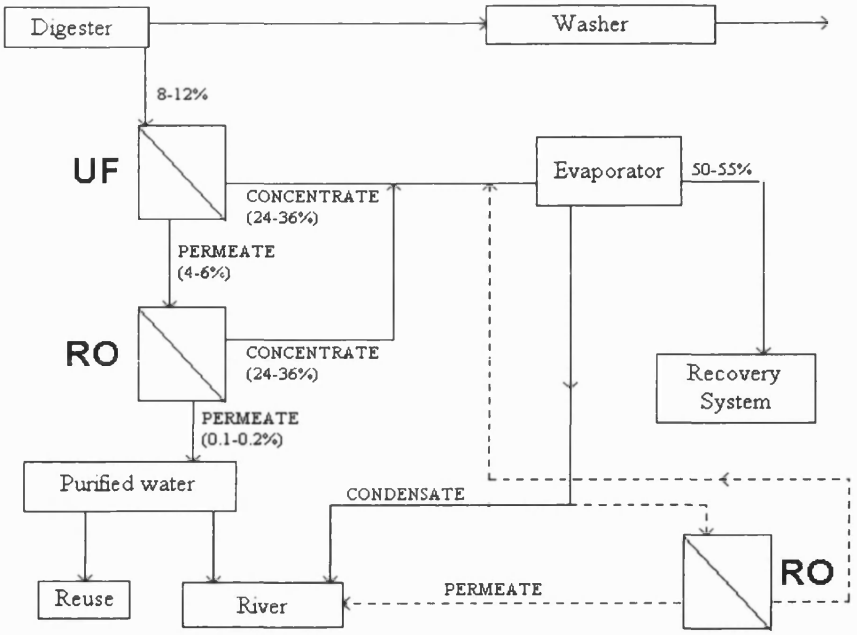


Figure 2.4: UF and RO separation system (adapted from Paulson and Spatz 1983)

Table 2.2: Energy consumption comparison of different techniques (adapted from Paulson and Spatz 1983)

Technique	Energy consumption for water removed
4-effect Evaporation	812 KJ/kg
Vapor recompression evaporation	360 KJ/kg
UF	93 KJ/kg
RO	123 KJ/kg
UF/RO Total	214 KJ/kg

2.3.1 Fractionation of spent sulphite liquor

With simple ultrafiltration, it is only possible to obtain a lignosulphonate purity of approximately 80%. In combination with diafiltration a concentrate of 25% total

solids containing 95% lignosulfonates is produced, *Jönssen and Wimmerstedt* 1985.

The UF permeate, containing low molar mass lignosulphonates, sugar and salts, is recycled to the chemical recovery system for evaporation and combustion (see Figure 2.4). For sulphite pulp mills without a recovery and combustion system, the full usage of the sulphite pulp components is crucial.

For instance, at Borregaard Industries, Norway, the lignosulphonates are used for the production of vanillin. Therefore a clean feedstock is necessary to produce vanillin economically in a special plant. This is done by UF combined with diafiltration (DF). UF removes the low molar mass constituents, which have a tendency to reduce the capacity of the vanillin plant.

2.3.2 The utilisation of spent sulphite liquor

The sugar fraction

Alcohol is produced from hexoses by anaerobic fermentation. This process has been used for a long time, but only the hexoses are utilised and the other sugars remain in the liquor. The alcohol is separated by distillation.

To also consume pentoses and other sugars, fermentation with a certain yeast is applied (known as pekilo-fermentation). If the fermentation time is long enough, more than 99% of the sugar can be consumed. The resulting cell-mass, which contains 50-60% protein, is separated from the remaining spent sulphite liquor (SSL) by filtration and used as animal feed. *Forss et al.1979* have pointed out the advantage of pekilo-fermentation prior to ultrafiltration, since carbohydrates and acetic acid is removed.

Lignosulphonate fraction

Lignin in sulphonated form has been available as an industrial raw material since 1886. But it was only in 1922 that the pulp and paper industry realised the waste

and pollution potential of lignosulphonates, (*Browning* 1975). Since then, lignosulphonates have been subject to worldwide research to find useful applications for them, *Claussen* 1981.

Nowadays, the production of sulphite pulp is decreasing. In 1988 the sulphite pulp was still 2,652,000 tons per annum, but had dropped to 533,000 tons in 1998, (*Stepanov* 2000). This is due to the Kraft pulping process being more efficient for papermaking. The lignin demand on the other hand is in increase and was estimated in 1998 to 1.1 million ton/year, *Anon* 1997.

LS are to be used as industrial detergents, dispersants, precipitates, binders and adhesives, for example animal feed pellets. Pure fractions of lignosulphonates are necessary for the production of vanillin, dispersants and adhesives.

2.3.3 System performance

The costs for a UF membrane system are mainly dependent upon the membrane area, permeate flow and purity of the lignosulphonates required.

The feed stream enters the system (module) with a solute concentration c_f (kg m^{-3}) and flow rate q_f (m^3 s^{-1}). The solute is retained by the membrane to a certain extent whereas the solvent can freely pass through the membrane. The concentration in the permeate is c_p and the permeate flow rate is q_p and leaves the retentate behind with an increased retentate concentration c_r and a retentate flow rate q_r.

The recovery or yield (S) is defined as the fraction of the feed flow which passes through the membrane:

$$S \equiv \frac{q_p}{q_f} \qquad (1)$$

High feed volume reduction indicates to what extent the solution has increased in concentration: As a result the performance declines because the concentration of the less permeable component increases on the retentate side. This leads to a rapid decrease of the permeate flow. This decrease is mainly caused by a 10-fold increase of viscosity, *Claussen 1978*. The result is depicted in Figure 2.5, where

with increasing volume reduction of the feed, the performance declines because the concentration of the less permeable component increases.

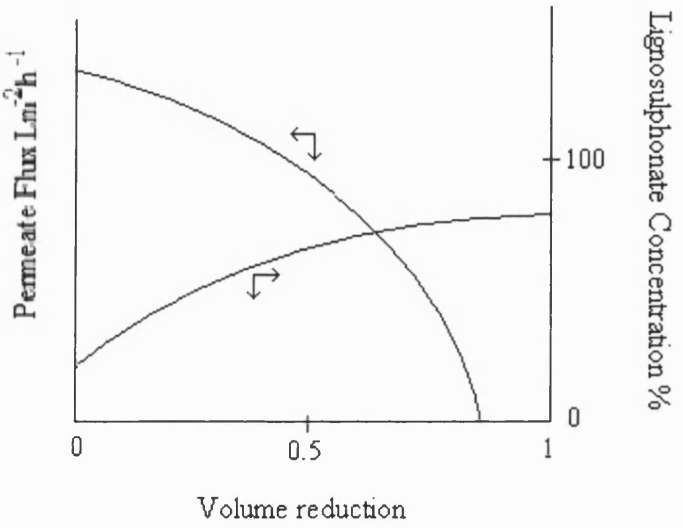


Figure 2.5: Lignosulphonate purity versus permeate flux (Claussen 1979)

Also, during concentration of the retentate, the rejections become negative, due to the build up of an „osmosis" zone of negative driving force, *Bansal* 1975.

To obtain a given lignosulphonate purity, the SSL is first ultrafiltered to a suitable conversion ratio. Then, when the permeate goes below a certain value and the process becomes uneconomic, which is at a conversion ratio of 0.75, water is added. This adding is continued at a constant solids level until the desired lignosulphonate purity is achieved.

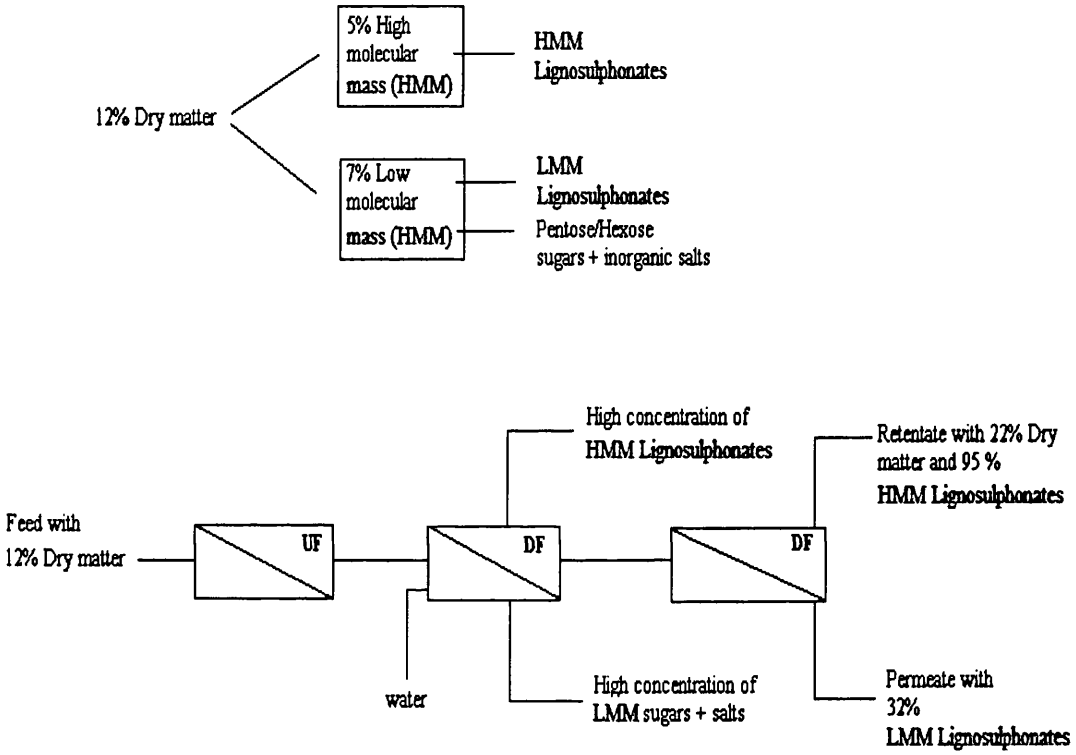


Figure 2.6: UF and DF of spent sulphite liquor

This process is called diafiltration (DF). The DF is necessary to remove mainly the sugar content, rather than the salt content. If fermentation is first applied as it can be seen in Figure 2.1, then a sufficient pure lignosulphonate fraction can be obtained with a significant reduction in the size of the ultrafiltration installation and wash water (Diafiltration water). Also the quality of the LS is equal to the LS obtained in the process without prefermentation, *Foss et al.* 1970. The reason why

certain companies still work without fermentation prior to UF could be due to heat energy present after the cooking of the wood chips.

The end product is a concentrate of 25% dry solids content with 93 % lignosulphonate purity. About 32% of the lignosulphonates are lost to the permeate. It is the low molecular mass fractions which are lost. In Figure 2.6 one can see a typical process characteristics for lignosulphonate fractionation and concentration.

2.3.4 Modules

Modules are necessary as a framework, in order to support the membrane and provide fluid management. The design of a module is crucial for the efficient running of membrane separation, since it determines energy consumption, ease of membrane replacement, provides fluid/fouling control and last but not least determines the performance of the cleaning step. It is important that the design is carried out properly in the first place, since after implementation any error causes a drastic drop in efficiency of the whole process.

Basically, four different designs are used for industrial applications. The first two are flat plate and spiral wound modules. Both are designed to host flat-sheet membranes. The other two are tubular and hollow-fibres. Both are designed to host tubular formed membranes. For further detailed information see *Mulder* 1996. All four concepts have certain advantages and disadvantages and are summarised in Table 2.3.

Table 2.3: Comparison of standard membrane modules

	Flat Plate	Spiral-Wound	Tubular	Hollow-Fibre
Packing-Density	Moderate	High	Low-Moderate	High
Energy-consumption	Low-Moderate (Laminar Flow)	Moderate (Spacer Losses)	High (Turbulent)	Low (Laminar/Dead-End)
Fluid-Management/ Fouling	Moderate	Good, if no particles poor, if particles	Good	Moderate-good (Lumen Feed) Moderate-Poor (Shell-side Feed)
Cleaning	Moderate	Can be difficult (blocked spacer)	Good-physical cleaning is possible. Backflush possible	Backflush Possible
Replacement	Sheet	Element	Tubes	Element
Manufacture	Simple	Complex	Simple	Moderate

2.3.5 The modules for usage in pulp and paper application

Spent sulphite liquor contains a great deal of fibres, which can be partly separated with a pre-filter, but a small amount will always pass the filter. Therefore it is important that the membrane module is so constructed that it will not be clogged by these fibres. This would occur with the compact and cheap spiral wound and externally pressurised hollow fine fibre modules. In comparison, tubular and plate and frame modules systems are not as sensitive to solid particles and both systems have been used for several years with spent sulphite liquors and Kraft liquors without problems, *Claussen* 1981.

For this study, a plate and frame module was developed. It offers research advantages over other modules, such as,

- cheap and simple to manufacture
- large range of membrane materials and pore sizes are commercially available
- membrane sheets can be easily replaced
- membrane sheets are supplied loose and not as elements, which eases analytical characterisation

2.3.6 Cross-flow or Dead-end

Conventional filtration processes operate in dead-end mode, where the flow is normal to the face of the filter, and the feed is forced through the membrane. This implies that the

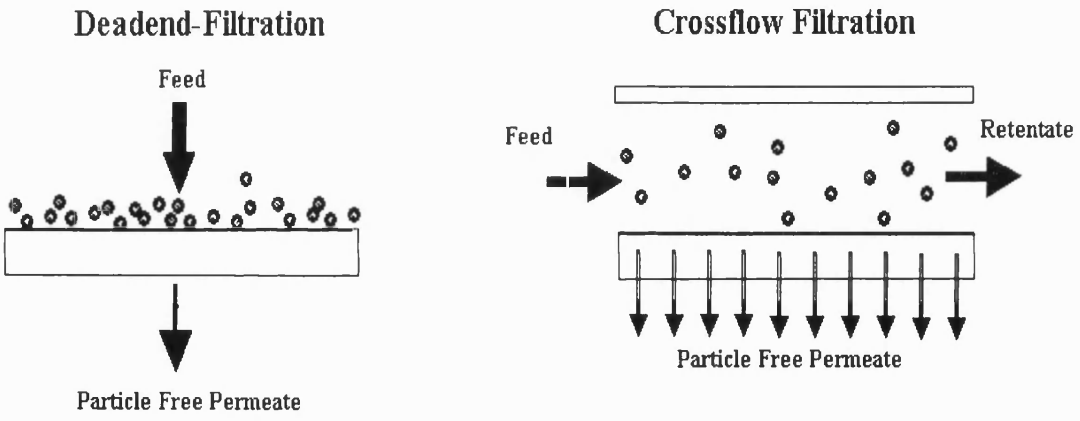


Figure 2.7: Schematic drawing of (left) dead-end and (right) cross flow filtration

concentration of rejected components in the feed increases and consequently the quality of the permeate decreases with time (*Mulder,* 1996).

Conventionally, UF is carried out in crossflow mode, with the principle flow parallel to the surface of the membrane. A simple cross-flow system concentrates the process feed by pumping it from a holding tank and across the membrane at the appropriate velocity, 1.0-8.0 ms^{-1} (*Coulson and Richardson*, 1991). The solvent permeates through the membrane and the feed emerges in a more concentrated form. The partially concentrated retentate is recycled to the tank for further processing, while the permeate is stored or discarded as required.

UF is carried out in both ways (Figure 2.7). For industrial applications however, cross-flow operation is preferred because of the lower fouling tendency relative to dead-end operation. The washing action of the fluid passing tangential to the surface of the membrane, ideally, keeps the filter from becoming clogged. Ideally, cross-flow operation would be a process without the deposition of material. The flux decrease occurring during crossflow UF shows that this is not the case. In practice the permeation rate falls with time due to concentration polarisation and membrane fouling phenomena.

2.4 Fouling in Ultrafiltration

Fouling can occur in all named membrane separations, but does not necessarily happen. It all depends upon the particular process and the feed material. In general, pressure driven processes for liquid separation are more susceptible to fouling than the others. In pervaporation or gas-separation, fouling is virtually absent. Therefore, the focus of this study is on one of the pressure driven processes, Ultrafiltration.

The interest in fouling is mainly driven by industry, which is loosing huge amounts of revenue due to the fouling problem. Two important criteria for separation efficiency are affected by fouling:

- **The Flux:** a loss of solvent flux with time.
- **The Retention:** a change in the composition or mass of the components retained by the membrane

The convective flux through a porous membrane is restricted by three factors:

$$Flux = \frac{Driving\ force}{Viscosity \bullet Total\ resistance}$$

which for Ultrafiltration becomes

$$J = \frac{\Delta P}{\eta R_{tot}} \qquad (2)$$

The resistance towards convective flow through a virgin membrane should be the resistance of the membrane only. In the absence of fouling, this should stay the only resistance towards flow. If fouling occurs, additional resistance is added, the so-called fouling resistance, R_f. This fouling resistance can be subdivided, into the different kinds of fouling resistances, depending on what mechanism has caused the fouling, like R_p for pore blocking or R_a for adsorption.

2.4.1 Reversible versus irreversible fouling

In Figure 2.8 various types of fouling are depicted. It should be noted that only concentration polarisation is reversible. Other types of fouling lead to permanent deposition of foulants on the surface or within the membrane structure and contribute permanently to the hydraulic resistance.

Concentration polarisation appears in UF, when a feed containing proteins or colloids is passing the membrane in crossflow mode. The retained solutes, which cannot pass the membrane, accumulate at the membrane surface where their concentration will gradually increase. Such a concentration build-up will generate a diffusive flow back to the bulk of the feed, but after a given period of time steady-state conditions will be established. The convective solute flow to the membrane surface will be balanced by the solute flux through the membrane plus the diffusive flow from the membrane surface to the bulk. See Figure 2.9.

Suppose that the flow conditions in the feed are such that at a distance δ from the membrane surface complete mixing still occurs (concentration c_b). However, near

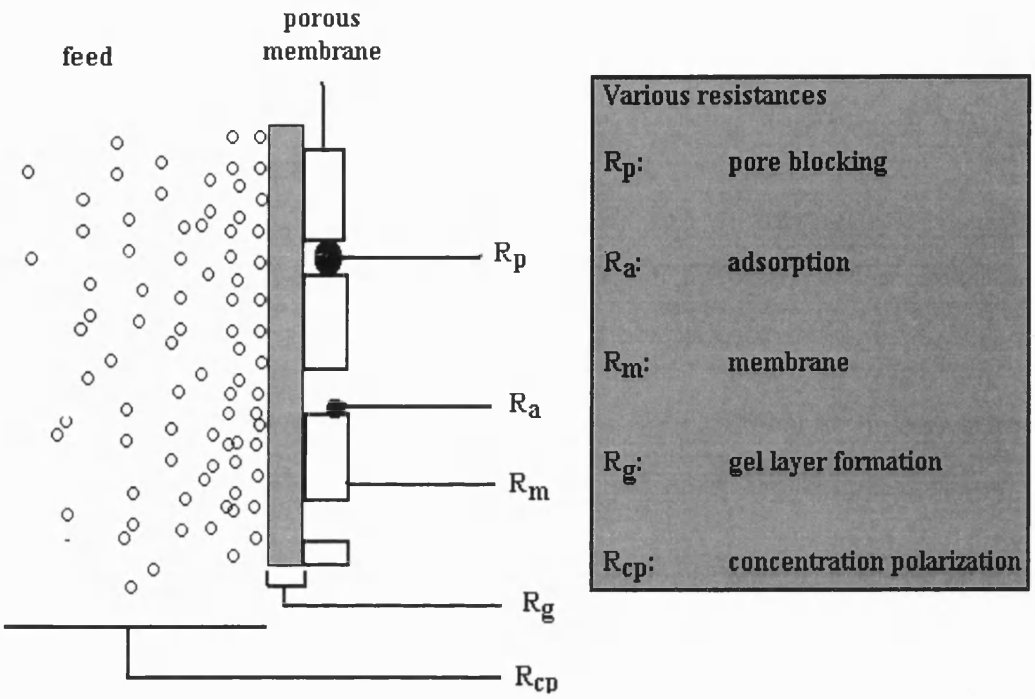


Figure 2.8.: Overview of various types of resistance towards mass transport across a membrane in pressure driven processes (Mulder, 1996).

the membrane surface a boundary layer is formed where the concentration increases and reaches a maximum value at the membrane surface (c_m). The convective flow of solutes towards the membrane may be written as; J·c. If the solute is not completely retained by the membrane, there will be a solute flow through the membrane equal to $J \cdot c_p$. The accumulation of solute at the membrane surface leads to a diffusive back flow towards the bulk of the feed. Steady-state conditions are reached when the convective transport of solute to the membrane is equal to the sum of the permeate flow plus the diffusive back transport of the solute, i.e.

$$Jc + D\frac{dc}{dx} = Jc_p \qquad (3)$$

(After *Mulder*, 1996)

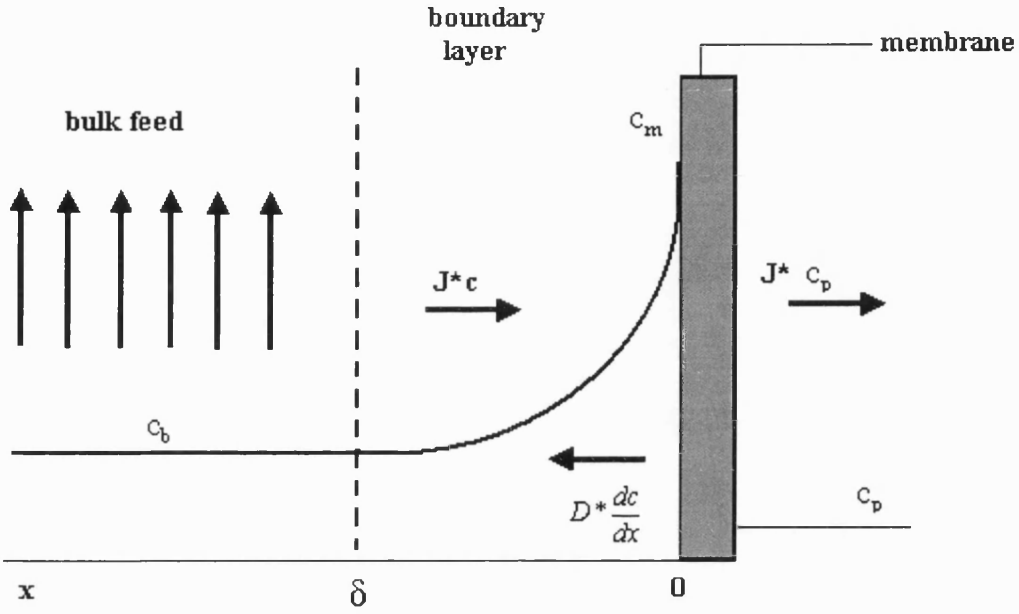


Figure 2.9: Concentration polarisation; concentration profile under steady-state condition

It is important to note that the accumulation of solutes near the membrane surface can trigger the build up of a permanent fouling layer. In the case of proteins and some colloids, the closer they get together near the surface the more likely it is that a gel-layer formation will occur which is a direct result of concentration polarisation.

For the filtration of spent sulphite liquor, the concentration polarisation effect has a large impact on permeate flow. Phenolic compounds such as lignosulphonate accumulating on the surface lead to a sharp increase of viscosity, hence reducing the flow through the membrane drastically. It is, therefore, important to run the process at temperatures as high as possible, sometimes at the maximum temperature limit the membrane can withstand. Another method to keep the concentration in an acceptable range, is diafiltration, as already described earlier. Even when operation is carried out under favourable conditions, the formation of

a cake or gel layer cannot be avoided. In fact, the gel layer is stated by other researchers as the dominant resistance towards flow in LS separation, *Woerner 1983 and Tsapiuk et al.* 2002. The studies claim that the cake layer is forming a „dynamic" membrane in addition to the polymeric UF membrane, which becomes the dominant force regarding separation, which means the gel layer determines the separation characteristic, not the selective layer of the UF membrane. That means cleaning would target this gel-layer, and over the long term, the cleaning agent would modify the structure of this gel-layer, influencing the separation performance, depending on the selection of cleaning agent.

2.5 The film-layer model

The separation performance of UF membranes, when separating wood pulp liquors like Kraft Lignin or Sulphate Lignin can be described by the film model, *Bodzek et al.* 1980 *Woerner et al.* 1984 and 1987 and *Tsapiuk et al.* 1989, 1993 and 2002.

The forming of a film or gel layer on the membrane surface is triggered by concentration polarisation described earlier. The CP in UF can be severe, since the flux through the membrane is normally quite high, the diffusivity of the macromolecule is rather low and the retention is very high. As a result the macromolecule accumulates on the membrane surface and may reach a limit concentration, when a steady state is reached and the back diffusion equals convection through the membrane. The macromolecules can interact with each other and can form, depending on size, shape, chemical structure and degree of solvation, a gel layer. This gel layer can be reversible or irreversible, again depending on the type of gel.

During constant pressure ultrafiltration of a macromolecular solution, the flux through the membrane will decline as long as the maximum or limiting concentration at the membrane surface is not reached. Once this concentration is reached, the flux becomes stable and the gel layer becomes the limiting factor determining flow, and cannot improve by raising the pressure. An increase in pressure will result in an increase of gel layer thickness or compaction, and

therefore resistance, but not higher fluxes. The major fouling resistance is then only the resistance inflicted by the gel layer.

The solute mass balance in the boundary layer can be described according to equation (3), see also Figure 2.9,

or

$$J(c - c_p) = -D\frac{\delta c}{\delta x} \tag{3.1}$$

with the boundary conditions

$x = 0 \rightarrow c = c_m$

$x = \delta \rightarrow c = c_b$ and after integration, equation 3.1 becomes

$$\ln\frac{c_m - c_p}{c_b - c_p} = \frac{J\,\delta}{D} \tag{3.2}$$

the ratio D/δ is the mass transfer coefficient k_s for the solute s. When the solute passage is low and tends to zero, $c_p \rightarrow 0$, so

$$J = k_s \ln\left(\frac{c_m}{c_b}\right) \tag{3.3}$$

Equation 3.3 is the key equation for the so called film model. With the knowledge that the gel layer is the dominant fouling resistance, equation (3.3) can also be described with equation (2),

$$J = k \ln\left(\frac{c_g}{c_b}\right) = \frac{\Delta P}{\eta(R_m + R_g)} \tag{3.4}$$

Due to the form of equation 3.3, J can be plotted as a function of ln (c_b). The result must be a straight line, with the slope being the mass transfer coefficient k. If it is assumed that the gel concentration remains constant across the gel layer, the intercept of the straight line on the abscissa (J=0) will give the value of ln (c_g), as depicted in Figure 2.10.

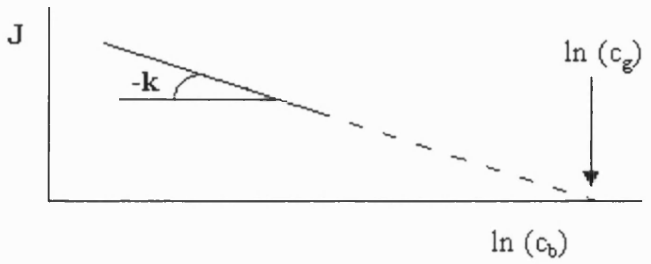


Figure 2.10: Limiting flux plotted as a function of the logarithm of the concentration of the bulk feed.

2.5.1 Film model for the ultrafiltration of wood pulp

As significant as it is, the film model has some drawbacks. In the literature the gel concentration c_g is not a constant, but rather depends on the bulk concentration and cross flow velocity. Different authors very often report varying values for a given solute. Furthermore, k is assumed to be a constant whereas the diffusivity of the macromolecular solute is often concentration-dependent.

However, as already mentioned before, the film model was found quite suitable by various researchers over the last two decades to describe ultrafiltration of wood pulp species, in particular Kraft lignin and lignin sulphonate liquors. A comprehensive study was done by *Woerner and McCarthy* 1984 and 1987 to investigate the drawbacks of applying the film model to ultrafiltration of these pulp mill liquors. They found that the concentration of c_g is independent of the Kraft lignin-to-solids ratio, softwood species, transmembrane pressure, mass transfer coefficient, temperature, pore size, and pH of the solution. The study on lignin sulphonates was less comprehensive, but pressure, softwood species and mass transfer coefficient were investigated and found not to influence the value of c_g. Since Kraft lignin and lignin sulphonates are very similar in chemical structure it suggests strongly that also the other parameters will not influence the value. In the study for lignosulphonates, the gel concentration was calculated with 265 g/L.

2.6 Factors affecting fouling in pressure driven membrane systems

The attempt to understand and hence reduce fouling problems in pressure driven membrane systems is a complex task, because to fouling is affected by a great number of parameters. Knowledge of biology, chemistry or engineering is necessary for understanding the problem as a whole. A full list of parameters affecting fouling can be seen in Figure 2.11.

Even though research into fouling has taken place for decades, many problems are still poorly understood. Research is carried out in two principal ways.

- **Model foulants**: have the advantage of helping to understand certain phenomena in a scientific way, since they are easy to reproduce and easy to characterise. The disadvantage is that the knowledge obtained is hard to transfer to separation problems with more than one foulants, *Mänttäri et al.* 2000.
- **Real liquor:** the disadvantage is that the composition is often too complex to understand the chemistry of fouling, but significant trends can be transferred to industrial systems.

Due to this complexity of fouling, certain parameters must kept as „Black boxes". That means when carrying out an experimental study many parameters must be kept constant whilst changing certain parameters of interest.

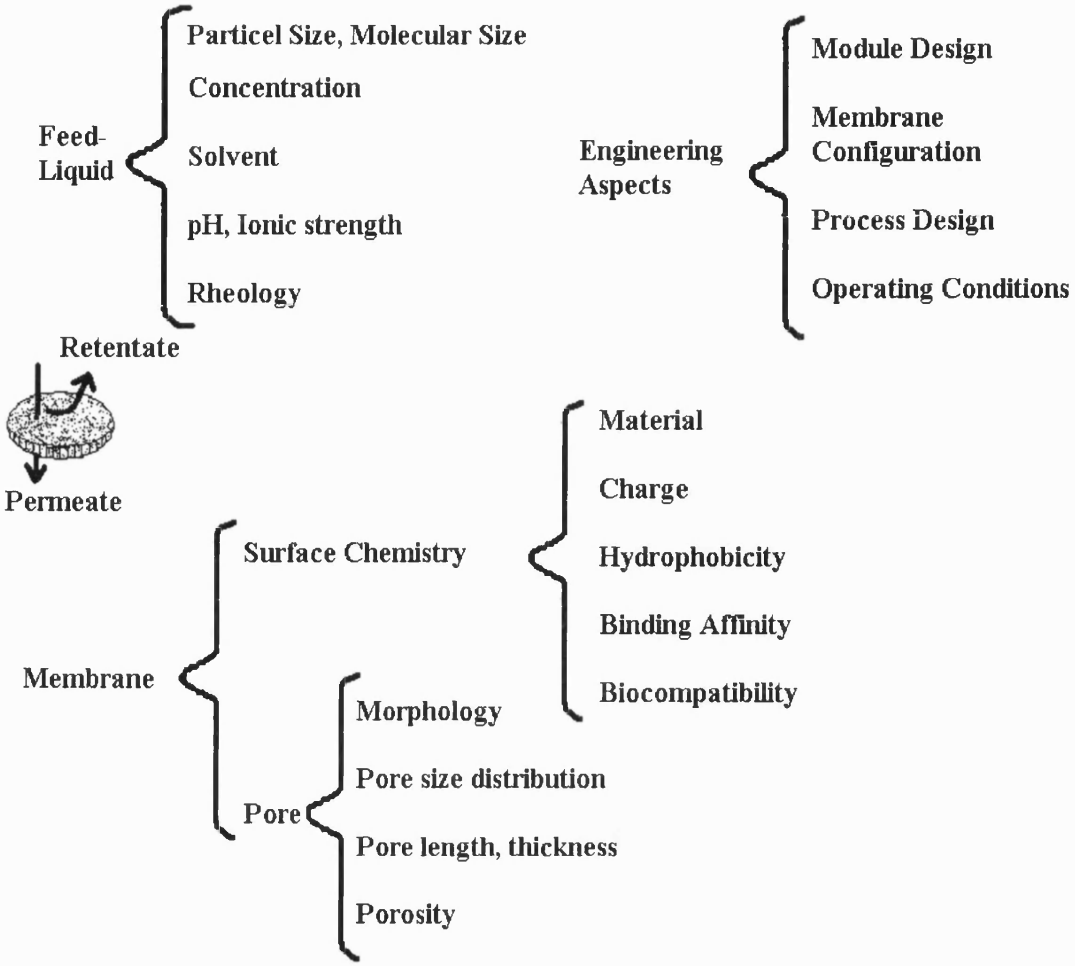


Figure 2.11: Factors affecting fouling in pressure driven membrane systems (after Nakamura 2002)

For this study it was decided to focus on separation with the real wood pulp liquor, because enough model studies have been done on the major foulants, such as fatty and resin acids. Also, as has been already shown, there is good data available concerning the type of fouling, when ultrafiltering wood pulp liquors. But only a little knowledge is available concerning the cleaning of these types of fouled membranes, and therefore, the focus of this study is on chemical cleaning and its long term implications.

2.7 Methods to evaluate fouling

In the past a vast amount of research has been carried out to develop or to identify suitable tools to investigate fouling upon membranes. Almost all of them can only be applied *ex situ*. That means the membrane under study needs to be removed from the test cell and specially prepared before undergoing investigation. These indirect methods of study include visual inspection, either with the naked eye or with the help of microscopy (e.g. atomic force microscopy, *Bowen and Doneva* 2000) and spectroscopic methods, like Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR), *Kim et al.* 1997 and *Zhu and Nyström* 1998. For surface characterisation, the methods of choice are contact angle for wettability (*Zhang* 1989) and zeta-potential for surface charge, *Nyström et al.* 1994, 1997 and *Pontié et al.* 1997. For an overview see Table 2.4 or *Lindau* 1995. The removal from the test-cell might cause artefacts or even destroy the fouling layer, so results obtained with these methods must be treated with caution. Due to these problems, research is moving towards tools which can monitor the fouling *in-situ* or online. But despite the drawbacks, results obtained with these *ex-situ* methods can still be vital for the understanding of fouling and cleaning. Therefore the following methods have been used:

- ATR-FTIR-Spectroscopy
- Atomic-Force Microscopy
- Extraction of foulants
- Contact angle measurement
- Zeta-potential measurement

Beside these tools, the researcher can also directly extract information from the filtration data itself, like product flow permeation, pure water flux and retention. With mathematical filtration models developed and extended by many researchers over the past decades, one should already be able to detect the type of fouling, like complete, standard blocking or cake formation, *Field et al*, 1995. In fact, the interpretation of filtration data is still the most important, since it directly shows directly the effect of parameter change.

Methods	Aim	Principle	Advantage/Disadvantage
ATR-FTIR Attenuated total Reflection-Fourier Transform Infra-Red Spectroscopy	To characterise the bulk and surface composition (functional groups) of membranes and fouling layers	The IR waves are directed through a highly refractive crystal which does not adsorb in the infrared region. With each reflection, certain wavelengths are adsorbed by the sample.	• To analyse the fouling layer, it must be different and thicker than the membrane material • Change of constitution during drying process.
EDX Energy Disperse X-ray Analysis	For the quantitative and qualitative elemental composition of the topmost layer of the sample (Fouling layer).	The sample is irradiated with high-energy X-rays, which produce photoelectrons from the core electrons in the sample. The *binding energy* is characteristic for elements. The *intensity* does not only depend on the element but also on the number of atoms in the sample.	• Depth of analysis is 1-3 micrometers. • Only atoms with atomic number higher than 11 are easily detected. The heavier the element the easier it appears in the image.
AFM Atomic Force Microscopy	Surface roughness, (pore size and numbers in addition to other measurements) and adsorption forces!	A tungsten or SiO_2 tip is moved over a sample surface. The interatomic forces between sample and tip vary from place to place and a deflection can be observed and measured	• The shape and size of the tip limits the size of the pores that can be measured

Table 2.4: Various analytical methods

Table 2.4: Various analytical methods(continued from previous page)

Methods	**Aim**	**Principle**	**Advantage/Disadvantage**
Contact-angle measurements	to detect changes in hydrophilicity of virgin, fouled and cleaned membranes	a drop of water is placed on a surface and the angle is measured between the surface and drop. The higher the angle, the less hydrophilic the surface is	• easy to apply • results vary with membrane a lot, due to porosity and roughness of the surface
Extraction	to analyse and quantify hydro-phobic species precipitated on the membrane	pieces of fouled membrane are treated with organic solvents to extract foulants and then to analyse in the GC	• type and quantity of foulants can be detected • the type and quantity depends strongly on the solvent used for extraction.
zeta-potential	to detect changes in membrane surface charges of virgin, fouled and cleaned membranes	every surface has a charge. The counter-ions accumulating at the surface charge can be moved by applying pressure through the pores. The amount of counter-ions can be measured and give the zeta-potential at different pH.	• easy to apply • results are relative results, and therefore difficult to interpret, since small pores give different values and the different mathematical models give way for different interpretation.

2.7.1 Flux measurements

Ex-situ characterisation methods help in understanding the composition of the fouling material, the location and surface chemistry. These analytical methods can be used to verify direct filtration data. Despite the success with analytical tools, like ATR-FTIR, filtration data already delivers a good understanding of what is happening. In the literature, fouling and subsequent cleaning has been evaluated by measuring pure water flux, product flux and retention.

Initially only pure water flux was used to evaluate the degree of fouling, but it was already recommended by *Trägårdh* in 1989 that the performance of cleaning should be measured by recording the flux when the membrane is exposed to the feed solution. Unfortunately, the product flux is only a tool, when at least two cycles are carried out. But because it is common practise for researchers investigating fouling to do only one fouling cycle, data about subsequent product fluxes can hardly be found in the literature.

The product flux performance can be measured in two modes:

- Constant Flux operation: when the flux is held constant, the TMP increases as the membrane fouls, and
- Constant Transmembrane Pressure operation: when the TMP is held constant, the flux decreases as membrane fouls.

In general, constant transmembrane pressure operation is used for laboratory-scale experiments. In industry a constant flux is necessary to maintain a certain output. It is thought that fouling in laboratory scale apparatus is very different from that in industrial operation. However, it is not clear how different. Another problem in constant flux operation is that the increase in pressure causes a denser cake layer with a higher resistance, *Rabie* 2001. In order to maintain a rather uniform cake layer, the separation was stopped as soon as a plateau was reached. In order to achieve this a constant pressure method was applied. There are two ways known to characterise the degree of fouling with the help of the product flux, *Liikanen* 2002.

$$Flux\ recovery = \frac{Flux\ after\ cleaning\ procedure}{Initial\ product\ flux\ of\ virgin\ membrane} \quad (4)$$

$$Fouling\ ratio = \frac{Steady-state\ product\ flux}{Product\ flux\ of\ virgin\ membrane} \quad (5)$$

The pure water flux is a recognised method in membrane science to quantify the quality of cleaning. In fact, the pure water flux measurements are essential for example at an early stage of the fouling process when there is no product flux decline detectable, but the adsorption of foulants has already started. Or, when the gel-layer has been established as the dominant factor for separation, and fouling can hardly be seen by just measuring the product flux. And finally, when hydrophilising agents are adsorbed (especially small amounts), this can be measured most easily with the PWF, *Maartens* 2002. Three different ways exist to calculate results, *Mänttäri* 2000:

$$Reduction of\ pure water\ flux(PWF) = PWF(before Filt.) - \frac{PWF(after Filt.)}{PWF(before Filt.)} \quad (6)$$

In model substance filtration tests, the PWF is mixed up with the product flux for the calculation of the reduction during model substance filtration.

Flux reduction of model substance filtration
= PWF (before filtration) - stabilised model substance flux (7)

In addition a definition of relative flux can be given as further info:

$$Relative\ Flux = \frac{Permeate\ flux\ at\ steady-state}{Pure\ water\ flux\ before\ filtration} \quad (8)$$

The advantage of using PWF in comparison to product fluxes is the possibility to use flux corrections with the help of viscosities.

In this study for fouling and cleaning evaluation, equations (4,5) and (6) are used.

2.7.2 Retention

If an aqueous solution is passed over a membrane, the solute is partly or completely retained while the solvent (water) molecules pass freely through the membrane. The degree of solute is passing determines the retention. It is given by

$$Retention = \sigma_r = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f}$$

where c_f is the solute concentration in the feed and c_p is the solute concentration in the permeate. The retention is a dimensionless parameter, *Mulder* 1996. The retention of solutes is an important parameter to identify the quality of product flux after cleaning. The value gives vital information about the progress of fouling, and to which degree cleaning is enhancing or avoiding further fouling. However, when the product concentration of the permeate is compared to that of the feed it turns out that the concentration factor is extremely high. In fact for Kraft lignin and lignin sulphates the effect of various process parameters is well investigated. *Woerner and Mc Carthy* 1984 and 1987 found that TMP, pH and the ionic strength of the feed solution have a strong influence on retention.

- pH: decreasing pH to acidic values increases the rejection coefficient. The more alkaline, the higher the average molar mass permeating through the membrane. It is thought that decreasing the pH will decrease the intermolecular association between lignin species as the phenolic hydroxyls protonate.
- TMP: the higher the pressure, the more the alkalinity affects the rejection towards lower values. In general, the higher the pressure, the lower the average molar mass permeating through.
- Ionic strength: decreasing the ionic strength leads to a moderate increase of rejection. The molar mass in opposite was strongly affected. Large molecules that are able to permeate the membrane at high ionic strength are almost completely rejected at low ionic strength.

As expected the rejection coefficient is strongly affected by the pore size, but this dependency lessens as the solute concentration is increased. This is likely due to

the gel layer forming on the membrane surface, which is promoted by the bulk concentration of lignin. The effect of the gel layer on retention was investigated by *Tsapiuk et al.* 1989,1993 and 2002 independently from *Woerner and McCarty 1984 and 1987.* Tsapiuk comes to the conclusion that the gel layer becomes the main separation force. This means that the membrane becomes less responsible for the degree of retention and the gel layer increases its influence. For more open ultrafiltration membranes, the gel layer even becomes the main force determining retention, and above pressures of 12 bar no differences can be seen between tight and open UF membranes, and the gel layer is the only factor which determines retention. Also, the higher the operating pressure becomes, the lower becomes the average molar mass permeating through the membrane. This is in accordance with the findings of *Woerner.* The reason why more open UF membranes are more affected by the gel layer than tight membranes is almost certainly that the gel layer overlapping with pore entrances in open membranes has a bigger impact on flux than in comparison with tight membranes.

Finally, *Tsapiuk et al.* also investigated Donnan effects on retention. They found that surface charges play a significant role, when separating solutions with low bulk concentrations. When a limiting concentration was exceeded, Donnan effects no longer have impact on the retention. This should be considered when carrying out tests with model solutions. The limiting concentration in the bulk was established to be 50 g/L of lignin.

2.8 The nature of pulp deposits on membrane

The fouling material which is causing flux decline was of major interest when pulp and paper manufactures started to use membranes for separation of certain components, like lignans. Besides investigating the influence of operating parameters, *Woerner and McCarthy* 1984 also investigated the effect of major components, like oily residues (fatty acids) and removal of very large colloidal particles. They report that fouling caused by oily residues and large colloids is not the major reason and conclude that the main material is lignous material (phenolic

substances). This finding was confirmed by *Carlsson et al.* in 1998 and *Watkins et* al. in 1999.

Lignosulphonates are suggested as model substances, e.g *Nyström et al.* 1995 for evaluating various membrane modifications for pulp and paper applications. Many researchers have pointed out, that the lignosulphonate's participate mostly in the fouling process. A review of the research into lignosulphonates will be given. This research is focusing on the mechanisms underlining the use of lignosulphonates as adhesives and dispersants. These applications are still not well understood and the research so far pays little systematic attention to the colloid chemistry of lignosulphonates. Therefore one must be very careful in drawing generalised conclusions from these well conducted but specific experiments.

2.8.1 Lignosulphonate structure

While the exact structure of lignosulphonates is not known, it is believed that they are built of guiacyl-propyl units with the sulphate groups attached to the aliphatic chains. *Goring and Rezanowich 1958* investigated the relation between sulphonation and molar mass on solubility; they suggested that this depends on the molar mass and the rate of sulphonation. The higher the sulphates content the better the solubility.

Lignosulphonates are considered as polyelectrolytes. The work of *Gardon and Mason 1955* indicate that lignosulphonates can be considered as substances consisting of flexible chain molecules with ionisable groups attached to them.

1. In solution the molecular shape depends upon the net electrical charge of the molecule. In the uncharged state the molecule curls up. If the ionic groups are dissociated, the polyelectrolyte molecule extends owing to the electrostatic repulsion between neighbouring groups.
2. The degree of ionisation of lignosulphonate depends upon its concentration and also upon the presence of simple electrolytes.

These two rules leads to two different behaviours:

1. At low concentrations of LS, the molecules occupy only a small part of the solution: this favours the escape of counter-ions, leaving the LS charged and extended
2. At high concentrations of LS, the room between the LS chain becomes smaller, which hinders the escape of the counter-ions, leaving the LS uncharged and coiled.

The LS molecules can also lose their charge, even at low concentrations, if the concentration of the counter-ions in the free space is increased by the addition of simple electrolytes containing the same counter-ion as the solution. At low concentration of LS the molecules are curled and therefore the viscosity is smaller than at higher concentrations of LS, when the LS molecules are extended and charged.

2.8.2 Viscosity properties of Lignosulphonates

As *Gardon and Mason* 1955 reported that at low LS concentration, a decrease in ionic strength results in extending of the LS molecules, and therefore in an increase in the hydrodynamic volume occupied of the molecules in water.

The viscosity depends on the concentration of solid content. For instance, the viscosity for a 40% solid sample is over 100 kCp. It does not matter if the LS molecule are from softwood or hardwood pulps. Raising the temperature proved to have a significant effect on slowing the rate of gel formation. Change of viscosity by caustic addition was not significant. The gelation could be enhanced substantially by the addition of diepoxides and epichlorohydrin. If Ca LS are used the viscosity is very high (alkaly), if pure LS are used, gained by ion exchange, the viscosity is very low. Obviously at alkali conditions the Ca ion will hold together a matrix of LS micelles to form a gel. Unlike pectin the gel cannot be formed by the addition of Calcium-ion; the Calcium has to be in a matrix as

obtained during pulping. When Ca was simply added back or to pure LS only precipitation occurred, but not forming of a gel (*Collins et al. 1977)*. A similar result was found by *Nyman 1986*, who coagulated pure LS, by addition of Ca. But the amount of Ca was very high and observed to be much higher in comparison to coagulate Kraft Lignins. In addition, *Nyman* found that addition of NaCl did not induce coagulation at all of LS at any pH, but an increase of ionic strength decreased significantly the pKa (value for dissociation) value of the solution. This agrees completely with *Kontturi* 1988, who found that for NaCl the diffusivity of lignosulphonate increases with increasing salt concentration, and the effective degree of dissociation increases with decreasing salt concentration. In the case of 2:1 electrolytes ($MgCl_2$) the behaviour is slightly different at very high salt concentrations. *Askvik et al. 1999* made surface tension experiments with lignosulphonate and sodium chloride and found out, that the surface tension decreases linearly when adding sodium chloride. They also carried out experiments with pure lignosulfonates and examined their surface tension. They showed that the higher the average molar mass the higher the surface tension. These phenomena of decreasing surface tension when increasing sodium chloride could be perhaps explained by the increased dissociation of the lignosulphonates, which lowers the molar mass distribution and therefore the surface tension.

Other ions like Fe can also bind to LS and is said to be responsible for the colour of the molecule. Indeed a precipitation of LS leads to a significant drop in the colour of the pulp.

Another important observation is that with removal of Ca ions from Ca-LS the molar mass decreased dramatically by about 50% (*Collins 1977)*. To explain this, the investigation from *Rezanowich 1960* must be cited. He claimed that the LS molecule can be assumed to be made of crosslinked, polyaromatic chains that are randomly coiled in the unexpanded state, see Figure 2.12.

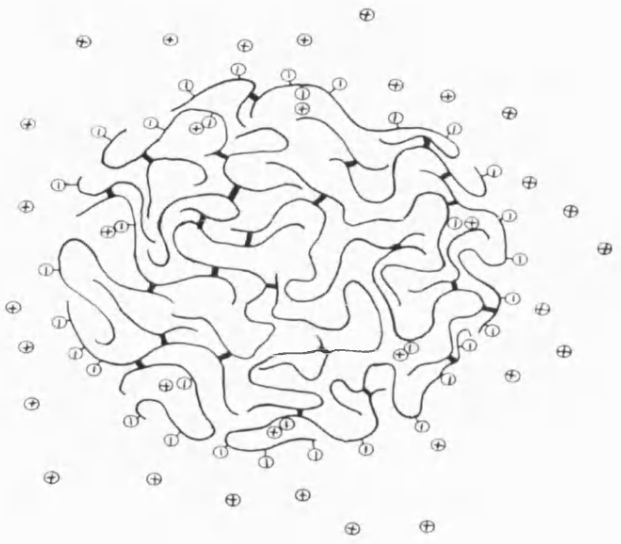


Figure 2.12: An idealised model of the lignosulphonate molecule in solution. Adapted from Rezanowich 1960

Kontturi 1988 in agreement with this model also suggests that the lignosulphonate molecule in solution can be assumed to be a sphere. The negatively charged sulphonate groups are mainly on the surface or near the surface of the particle. A double layer of counter-ions (Na, Ca) is present in the solvent nearby the LS. If the amount of counter-ions are decreased, the negatively charged ionic groups are set free, which cause a rejection of other LS and the conglomerate of randomly coiled chains can fall apart. This theory is supported by the finding of *Collins et al.* as stated above, that at alkalic conditions the Ca ion will hold together a matrix of LS micelles to form a gel. But it must be emphasised that it is still not clear at which scale the metal ions are responsible for the sticking together of the LS-polymer. Perhaps single charged counter ions only reduce the surface charge but double charged counter ions are able to build bridges. The question is: are fractions composed of molecular aggregates held together by strong association forces or are they real macromolecular species, *Lindberg et al.* 1965. In contrast to this, the standard model „microgel", has a lot of restrictions according to *Afanasjev et al.* ***1997***, which cannot explain all properties. He and his co-workers claim that for a sodium lignosulphonate one can not expect a three-dimensional

structure, even at high molar masses. Due to their experimental approach they conclude that the sodium LS represent chaotic branched chains for molar masses over 10kD. Further it is said that the chains are rigid. This might be true, but the investigators haven't discussed the relationship between cations and the network. Therefore the question arises, what is the situation for calcium LS, or sodium LS with a higher cationic content. Based on this, *Rezanowich* hypothesis could still be valid under certain conditions.

2.8.3 Interaction between Lignosulfonates and simple metal ions

1. **Molar mass**: the ion exclusion is increased the lower the molar mass and the lower the concentration of the LS. This seems to be related to the findings of *Gardon and Mason 1955* that the degree of ionisation of lignosulphonate depends on its concentration and also upon the presence of simple electrolytes and that at low concentration of LS, the molecules occupy only a small part of the solution: this favours the escape of counterions, leaving the LS charged and extended.

The difference in dissociation becomes smaller at high molar masses and it is reported to vanish at very high molar masses, *Eisenberg* 1960. The investigation of *Lindström* 1976 showed that the dependence of dissociation upon concentration was only found for Sodium lignosulphonate at a molar mass of 6kD.

2. **Specific ion interaction**: the binding order for a LS-sample of molar mass of 12 kD is $Ca^{++} >> Li^{+} > Na^{+} > K^{+}$. The binding order was found to be the same as it was for polyphosphates. This indicates that Ca-LS dissociates on a much lower scale than monovalent LS-salts.

Since Ca binds more strongly to the LS it could give some conclusions to real „site-binding" effects with for example not only the sulphonate group, but also the aliphatic and phenolic hydroxyls and methoxy groups.

3. **Influence of salt concentration**: the higher the salt concentration, the higher the grade of dissociation.

2.9 The membranes

Whether a particular membrane can be used for a certain application is dependent on its capital cost and performance in terms of flux and retention. The performance can be greatly influenced by the temperature of the feed. The higher the temperature, the lower the viscosity and the diffusivities of the species increase.

The temperature of the fresh SSL is usually about 90°C and if the membrane could withstand this temperature, no cooling device would be needed, which would be a further advantage. Temperatures higher than 90°C can resisted only by inorganic membranes, which show a worse performance than organic membranes at lower temperatures of 70-80 °C. Since these inorganic membranes are much more expensive than organic ones, they are not used for SSL fractionation, *Eriksson* 1980.

The aim of this study is to generate sets of data with three different polymers of different hydrophilicity, which was achieved with the following materials:

Regenerate cellulose — Polysulphone — Polyethersulphone

Hydrophilic → → → → → **Hydrophobic**

Tabe 2.5: Condition and performance of different membrane materials (Bansal & Wiley 1975; Collins, Webb & Wiley 1975)

	Lifetime (Theory)	Lifetime (Practice)	Membrane costs
Cellulose-acetate(CA)	For pH below 3 and temperature highert than 30°C lifetime low.	With SSL at 55°C for over 1000 h without problems	Cheap, but used for only certain applications, since not capable to withstand cleaning
Polysulphone (PSf) or Polyether-sulphone(PES)	Can withstand 80°C continues-ly and extreme pH	2-3 years	2-3 times more expensive than CA membranes

2.9.1 Cellulose acetate membrane

Per unit area, cellulose acetate membranes are cheap, compared to other membranes. Theoretically they show a rather short lifetime for conditions at temperatures higher than 30°C and a pH below 3. In practise for the separation of spent sulphite liquor at 55°C they show a runtime of over 1000-hours, without detoriation. *Bansal* 1975 stated that this is due to a dynamic layer, which is formed by the lignosulphonates and protects the membrane. At the same time this dynamic layer becomes responsible for the separation characteristic of this membrane, like flux and retention of species. *Collins et al.* 1975 have used this observation to create „dynamic membranes". On porous plastic support layers he added sand and finally carbon particles. Within these carbon particles high molar mass fractions of LS form the selective layer. Such membranes have similar separation characteristics to cellulose acetate membrane, but have the advantage of withstanding high temperatures of 90°C.

However, to maintain a high flux, the membrane must be cleaned. This is normally done with an alkaline solution, which reduces the lifetime of the membrane considerably and makes this kind of membrane useless.

2.9.2 Polysulphone and Polyethersulphone membranes

Polysulphone membranes are three times more expensive than cellulose-acetate membranes, but can withstand temperatures at 80°C continuously (*Eriksson* 1980). An experimental investigation with polysulphone membranes with Cut-off values of 6 kD and 20 kD was just done to examine feasibility, but gives no information about membrane lifetime and cleaning behaviour.

2.9.3 Inorganic membranes

Mineral membranes made out of metal oxides show good performance for SSL fractionation. They can be treated under harsh acidic/alkaline and reducing/oxidising conditions in order to clean them, which can lead to nearly

100% recovery of pure water flux. The operating temperature is only limited by the chemistry of the concentrates (e.g. polymerisation reaction) and solvent.

The disadvantage is the capital cost for these kinds of membranes, which is still a multiple of what it is for polymeric membranes. As stated above, it is highly questionable if harsh cleaning environments, can bring an economic benefit when run for long time, since some polymeric membranes can also take extreme pH and temperature conditions. Therefore, the focus in this project will remain on polymeric membranes.

2.10 The cleaning procedure

Cleaning procedures depend upon internal membrane characteristics, such as

- pore size
- Pore size distribution
- Pore density
- Membrane material (hydrophilicity, charge...)

as well as external parameters of the cleaning process, like

- Temperature of solution
- Concentration of cleaning agent
- Type of cleaning agent
- Flow velocity

There are many parameters, which have to be optimised to reach a successful cleaning, but the internal parameters are fixed and to a large extent determined by the separation process. Even the choice of membrane material is very restricted, since there are only a few polymers in use, which are cheap and can resist harsh environments. The choice is further narrowed since certain materials are bound to certain membrane configurations, for instance inorganic membranes are not available as sheets, or membrane manufacturers offer a limited range of materials.

Lindau et al. 1995 pointed out that the pure water flux can be regained even if the foulants are not completely removed. They observed with model foulants, that the fouling became more and more pronounced, but the water flux could be regained after each cleaning cycle. The research group emphasised due to their experience, that long-term experiments are necessary to get full understanding of cleaning processes. *Bowen and Gan* 1993 emphasised that internal pore blocking is a major reason for flux decline.

Another problem, which is related to fouling, is the concentration polarisation layer. In many cases, especially for high viscous solutions, the polarisation layer determines the performance. Furthermore it can dictate or initiate the fouling and long-term decline of flux (*Yao et al.* 1995).

For this study it was decided to investigate concentration, temperature and the type of cleaning agent. Of the internal parameters, the pore size, the distribution and density were not investigated. This is because there are already studies available on the influence of pore size on fouling. Furthermore, it is hard to control those internal parameters by using commercial membrane products. Even though membrane manufacturer offer different membrane materials with the same molar mass cut off, the pore size, density and distribution might differ. This is due to different manufacturing processes, which influence those parameters as well as the surface roughness (and therefore the shape of the pore entrances). Therefore, the ideal membrane for a scientific study would be self manufactured with known internal parameters. The process of manufacturing and the influencing parameters on certain membrane characteristics is still subject of research and would be a project in itself. Fortunately commercially available membranes can still be used

when making scientific studies, as long as they are manufactured by the same company, or more significantly are tested for their molar mass cut off with a standard method. When this target is met, a scientific investigation of the influence of the membrane material hydrophobicity can be carried out.

The remaining parameters of investigation are therefore:

- Membrane material
- Type of cleaning agent
- Concentration of cleaning agent
- Temperature of solution

2.10.1 Fouling and cleaning synergy

In order to speak about a relationship between the fouling step and the cleaning step, it seems to be useful to clarify the meaning of "Synergy":

ⓘ *Synergy is the cooperation and interaction of different factors and forces in such a way, that the commonly achieved impact is bigger than the sum achieved by the single ones. (Drosdowski 1985).*

Applied to this study it means that all the parameters influencing fouling and all the parameters influencing cleaning are potentially affecting each other. Furthermore it means in theory that every single parameter needs to be optimised in relation to other parameters. The sheer amount of influencing parameters makes it impossible to study all at once. Fortunately, as already stated, the fouling is well understood, in particular influencing process parameters like temperature, pressure and crossflow, and synergetic effects on cleaning have been studied by *Bartlett and Shorrock.* What remains is a lack of understanding how cleaning is influencing the subsequent fouling. *Shorrock* 1999 pointed out that for any kind of synergetic effect, the time factor is important. Studies over one cycle have limited

meaning. It is necessary to examine this interaction between fouling and cleaning over multiple operational cycles to enable any synergistic effects to be observed.

Some further considerations regarding synergy

Temperature of solution and flow velocity will most likely have a physico-chemical impact on the removal of the fouling material. Temperature and flow velocity will enhance the removal rate by increasing the mass transfer into the fouling layer and enhancing chemical reactions by providing kinetic or thermal energy.

Membrane material, type and concentration of cleaning agent will provide surface and chemical energy and will have a more immediate impact on modifying the fouling layer, its composition, morphology and hydrophobicity.

Synergistic effects can be of multiple nature regarding their cause. The reason why a synergy effect is observed is difficult to determine because of the large variety of interactions, but maybe a broad distinction is possible:

A synergetic effect will change the quality of cleaning and as a result the quantity of cleaning. In other words if the membrane or the fouling layer is chemically modified by the action of the cleaning agents, it will lead to a change in flux recovery and a long lasting effect. If the physical process parameters are changed, it will accordingly lead to a proportional change of flux recovery, but will have only an impact as long as the process parameters are not changed again. Therefore, effects caused by changing process parameters, such as temperature or crossflow, are likely to be short term.

This approach will be used as a matrix to explain the results regarding synergetic effects.

2.10.2 The choice of cleaning agents

The cleaning cycles were carried out with a widely used formulated cleaning agent, *P3 Ultrasil 11* (*Ecolab*), and with sodium hydroxide (*Fisher Scientific*). *P3*

Ultrasil 11 consists of sodium hydroxide (ca 44wt%), tetra sodium salt of *EDTA (>30wt%),* anionic surfactants (~5wt%), non-ionic surfactants (~5wt%).

The alkaline formulated *P3 Ultrasil 11* is known in industry as a good cleaning agent and is actually currently used in the pulp and paper industry, but there is little published information concerning the precise function of the ingredients during the cleaning process and how they interact. The use of combined cleaning agents was first studied by *Grasshoff* 1988, but there is still a lack of detailed investigation of their mechanism of action, *Gan et al.* 1999. Therefore, it will be of interest to study this especially in comparison to a single formulated cleaner over many cycles.

Ultrasil 11 contains sodium hydroxide to achieve the alkalinity, since it is thought that phenolic substances are more easily removed when under alkaline conditions. This is because of the second major ingredient Ethylen diamine tetrasodium acid, better known in its short form EDTA. This substance has the function as complexing agent especially for divalent cations like Ca^{++} or Mg^{++}, which would otherwise bridge negative organic substances together and lead to a harder fouling layer. This chelating works the best under alkaline conditions, *Yoon et al. 1998.* Unfortunately the ability to complex heavy metal cations has brought EDTA into discredit, since it is thought that it will dissolve these heavy metal cations from the sediments in lakes and rivers, once it is released into the environment. The minor components of Ultrasil 11 are surfactants, which will solubilise foulants. But both surfactants, anionic and non-ionic, are also known to adsorb to the membrane material to a varying degree and change the membrane hydrophobicity. A short literature review will be given in order to help understand the forces at work during the cleaning of membranes. The focus will be on the interaction of surfactants with (polymeric-) surfaces and the interaction of polyelectrolytes (in this study lignosulphonates) with surfactants. Only the most significant features will be summarised. For more information see *Jönsson* et al. 1998.

2.11 Adsorption of surfactants at polymeric surfaces [According to Jönsson et a.1998]

The adsorption of surfactants depends strongly on the polarity of the polymer surface. If the surface is very hydrophobic, the surfactant will adsorb with their hydrophobic hydrocarbon moiety in contact with the surface and their hydrophilic moiety in contact with the solution, as shown in Figure 2.13(a). On very polar surfaces, on the other hand, the surfactants (at low solution concentrations) adsorb with their polar moiety in contact with the surface due to the interaction between the surfactant head group and the surface, Figure 2.13(b) upper case. At higher surfactant concentrations two different structures at the surface are possible. If there is a strong attraction between the surfactant head group and the surface a monolayer is formed, where the surfactant head groups are in contact with the surface and the hydrocarbon moieties are in contact with the solution. This adsorption structure will create a hydrophobic surface which in turn will adsorb further surfactants with the same configuration as described above for hydrophobic surfaces, which means a surfactant bilayer is formed at higher surfactant concentrations, Figure 2.13(b) lower case.

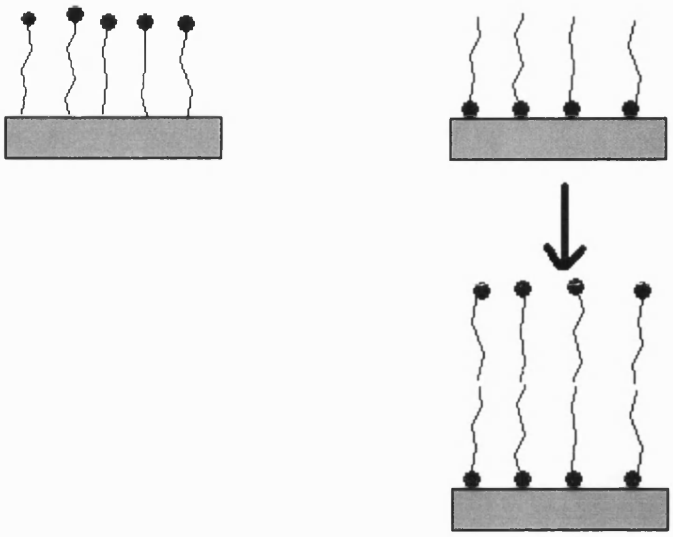


Figure 2.13: Surfactants adsorb (a) on non polar surfaces with their hydrocarbon part in contact with the surface as well as (b) on polar surfaces with their polar part towards the surface.(modified from Jönsson et al. 1998)

2.11.1 Ionic surfactants adsorb on hydrophobic surfaces

The amount of adsorbed ionic surfactant will depend on the chain length and number of branches. In general, the greater the number of hydrocarbon units, the greater the adsorption. Also, addition of salt will reduce electrostatic repulsion, hence increase the adsorption of surfactants with their hydrophobic parts towards the surface. The degree of adsorption is relatively insensitive to the polarity of the surface. What changes is the type of adsorption as described above.

2.11.2 Non-ionic surfactants adsorb on hydrophobic surfaces

The adsorption behaviour of non-ionic surfactants has very similar features compared to ionic surfactants. Most important, the degree of adsorption depends on the relation between the polar and non-polar parts, in other words, the bigger the hydrophobic part in relation to the polar part, the bigger is the tendency to adsorb on a hydrophobic surface.

But the overall tendency of non-ionic surfactants to adsorb is much greater than it is for ionic surfactants. This is due to the lack of electrostatic repulsion between the molecules at the surface. For instance, the critical micelle concentration of non-ionic surfactants is in general of the order 10-100 times smaller than those of ionic surfactants with the same hydrocarbon chain length. Also, the adsorbance of non-ionic surfactants is strongly temperature dependent. The higher the solution temperature, the higher the adsorption.

2.11.3 Ionic surfactants adsorb on hydrophilic surfaces

The adsorption of ionic surfactants at low concentrations on polar surfaces takes place almost exclusively by an ion exchange mechanism. The counter-ions along the surface are exchanged and replaced by the surfactants, which face with their head groups toward the surface. When the concentration of surfactants in the bulk is very high, a double layer is formed. Again, the degree of adsorption is driven by the surfactant alkyl chain length and only marginally by the interaction with the surface.

The adsorption of ionic surfactants on hydrophilic surfaces is almost completely independent of temperature.

2.11.4 Non-ionic surfactants adsorb on hydrophilic surfaces

The adsorption of non-ionic surfactants on hydrophilic surfaces is dictated by the interaction between the surface and the hydrophilic polyoxyethylene chain. If there is an interaction present, the adsorption behaviour will be similar to the adsorption of ionic surfactants on hydrophilic surfaces. But for non-ionic surfactants, the initial interaction is much more important than it is for ionic surfactants in order for the adsorption to take place. Because the interaction between the surfactant head group and the polar surface for the overall adsorption is so important the pH of the solution plays a major role. Under alkaline conditions, the amount of hydroxyl ions becomes so overwhelming that they compete for the adsorption sites and at pHs above ca. 10 all non-ionic surfactants with their weaker hydrophilic polyoxyethylene groups are displaced from the surface.

2.11.5 Mixture of anionic and non-ionic surfactants

Mixtures of anionic and non-ionic surfactants are very common in technical systems since these systems both give rise to electrostatic repulsion and steric repulsion between particles at which surfactants are adsorbed. As already mentioned, non-ionic surfactants have a much higher tendency to adsorb on surfaces than ionic surfactants. Even if the ionic/non-ionic relation in the bulk solution is 3 to 1, the surface will mainly adsorb the non-ionic ones.

2.12 Interaction of polymers with surfaces

The amount of polymers adsorbed on the surface depends on the molar mass of the polymer. In a polydisperse system the high molecular mass species will be preferentially adsorbed at the expense of the low molar mass species. Since the adsorbed amount is dependent on the molar mass, the system depends on the ratio of the polymer solution volume to the available surface area. A small area will adsorb only high molar mass species and a large area will also lower molar mass species. This is valid for neutral polymer and also for charged polymers, so called polyelectrolytes. For the latter group some additional laws of behaviour exist and will be explained in the following section.

2.12.1 Adsorption of Polyelectrolytes

The presence of charged groups in the polymer makes the adsorption behaviour more complex and shows some features similar to ionic surfactants. But in many cases, non-electrostatic forces govern the adsorption process, which becomes obvious when a negatively charged chain is adsorbed on a negatively charged surface. Adding a salt to the solution will enhance the adsorption process, since it will shield the repulsive, so that a phase separation is promoted. In this process divalent cations are far more effective in promoting this than cations with a single charge. Therefore the adsorption will also show a pH dependence. This could

come from a titration of the adsorbing surface and/or from a titration of the polyelectrolytes. That means, the higher the pH, the more negatively charged and the lower the adsorption.

The initial adsorption of polyelectrolytes is a fast process, but the approach to a true equilibrium situation can be very slow. This is due to rearrangement and/or adsorption/desorption of different molar mass species. Also, a polymer is in theory reversibly adsorbed, but practically be considered to be irreversibly adsorbed. This apparent contradiction is explained by the slow dynamics in a polymer system. In order for a polymer to desorb from a surface all the polymer segments that are attached to the surface must detach approximately at the same time. If only a few segments detach, there is a high probability that other segments will adsorb before the whole polymer desorbs. Thus, the polymer chain is grounded on the surface by its own inertia.

Table 2.6: Summary of adsorption of polymers and surfactants

	Adsorption of					
	Ionic Surfactant		**Non-ionic Surfactant**		**Polyelectrolyte**	
	Temperature		**Temperature**		**Temperature**	
	Low	**High**	**Low**	**High**	**Low**	**High**
Hydrophobic Membranes e.g. PES	yes	yes	**more** than ionic surfactants	**much more** than ionic surfactants	yes	yes
Hydrophilic Membrane e.g. RC	yes, temperature independent		No	No	yes, but small	yes, but small

In Table 2.6, one can find a summary of the adsorption behaviour of the surfactants and polymers used during fouling and cleaning on solid surfaces. Surely all three will also interact which each other once adsorbed at the surface. In general, surfactants adsorbing on hydrophobic surfaces will make the surface more hydrophilic and therefore repulse more polyelectrolytes (e.g. lignosulphonates). On the other hand, on hydrophilic surfaces with the surfactants adsorbing head towards surface, the surface will become more hydrophobic,

hence attracting even more polyelectrolytes. If the polyelectrolytes are allowed to adsorb first (e.g. if membranes are not conditioned with a cleaner and the fouling cycle is applied first), the surface will become even more hydrophobic and prepares the membrane for even bigger surfactant adsorption. The whole process of interaction will occur over many cycles and the interchange and interaction will eventually reach a steady state. The knowledge of these interactions will lead to the question of experimental design.

2.13 Experimental design

As already stated in the first chapter for the system studied here, there is little known about the chemistry of interaction between membranes, cleaning agents and fouling material. Also, the adsorption behaviour of surfactants described above is valid for solid surfaces. It is fair to say that this knowledge obtained for solid surfaces can be transferred to membranes, which are also solid surfaces but with pores in it. The above described rules of surfactant-surface interaction was already successfully proven to be also important for membrane surfactant interactions (*Doulia et al.* 1992 and 1997, *Field et al.* 1994 and *Chen et al.* 1992). In fact, there is evidence that the pores enlarge the surface area tremendously and hence the reaction area for the adsorption of surfactants on polymers. But the big difference between membranes and solid surfaces is that the modification of the surface will ultimately influence the performance. This can be determined with the measurement of two important parameters: the permeation of product and/or pure water flux through the membrane at a certain pH value and the rejection of matter known as the retention value. It is of great interest for industry and science how the choice of membrane and cleaning agent will affect the membrane separation performance over short and long term. This will have a direct impact on the economy of pressure driven membrane separation systems and will improve planning and scale-up of such systems to industrial capacity.

A summary of the experimental set-up can be find in Table 2.7 and 2.8. The main idea was how different membrane materials will perform when cleaned with different cleaning agents. The performance is studied with the permeation and

retention parameters. A cleaning agent was chosen Ultrasil 11, since it is know as an effective cleaner and also as it has been very successfully applied to our own cleaning studies over one cycle. Ultrasil 11 is a formulated cleaner with expensive components like EDTA and non-ionic surfactants. The following are more particular questions but in context still belong to the fundamental questions raised in the introductory chapter 1: (the numbers in front of each question relate to the question in chapter 1).

(1) *Synergy:* Which function and effect have the different components of Ultrasil 11 upon performance and how do they perform with different membrane materials?

(1) *Synergy*: Is a single formulated cleaner as effective as a multiple formulated cleaner? And if so, when is this the case and can the multiple formulated agent not be replaced by the single one.

(3) *Detection*: When(at which stage) are these components effective and efficient for the separation process ?

(2,4) *Differentiation*: How does temperature and concentration influence the cleaning performance over the short and long term?

Table 2.7 : Long term tests carried out in this study with different cleaning temperatures

		Long term test				
		Temperature low		Temperature high		
		NaOH	Ultrasil 11	NaOH	Ultrasil 11	Cleaning agent
Membrane Material	Polyethersulphone(PES)	√	√	√	√	Hydro-phob
	Polysulphone(PSf)	√	√			
	Regenerate Cellulose			√	√	Hydro-phil

Table 2.8: Overview over the optimisation work on short term fouled and long term fouled membranes, when Flux has reached a steady-state.

	Short term optimisation work						Long term optimisation at steady-state				
	Temperature		Concentration		Cross-Flow		Temperature		Concentration		
	NaOH	Ultrasil	NaOH	Ultrasil	NaOH	Ultrasil	NaOH	Ultrasil	NaOH	Ultrasil	Cleaning agent
Polyethersulphone(PES)	√	√	√	√	√	√	√	√	√	√	Hydro-phobic
Polysulphone(PSf)	√	√	√	√	√	√					
Regenerate Cellulose							√	√	√	√	Hydro-philic

2.14 Summary

This chapter dealt with the process and design considerations, which arise when using spent sulphite liquor for studying cleaning of membranes over multiple operational cycles. SSL was chosen for the study since it offers exceptional properties desired for the study, such as high fouling potential and microbiological stability and it is a product from the bulk industry for which the fouling problem is of particular importance. The basic principles of membrane separation processes for aqueous solutions and porous membranes are explained and advantages of this technology for the use in the pulp and paper industry are given, which are mainly based on energy and material saving (cost). One problem when SSL is fractionated and concentrated with UF membranes is the massive drop in performance due to increase of concentration and viscosity. To counter this problem a diafiltration needs to be applied. Modules in use in the pulp and paper industry are those which are less likely to be clogged by fibrous material, for example plate and frame or tubular configurations.

In the past, fouling in porous membrane has been intensively studied and is well understood, with methods developed to identify the location of the fouling resistance. Two important process criteria are affected by fouling, which are flux and retention. Concentration polarisation triggers the build up of a gel or film layer on the membrane surface, which determines the long-term separation performance.

In this study, the interpretation of filtration data over multiple operational fouling and cleaning cycles is supported by ex-situ analytical methods, such as ATR-FTIR, AFM, zeta potential and contact-angle measurements as well as extraction of foulants. A brief overview of these methods is given.

In the past researchers identified ligneous material as the main foulants rather than oily residues or large colloids. Therefore a literature review is given on the main ingredient of SSL, the lignosulphonates. LS are considered as polyelectrolytes and appear in solution as spheres. Under alkalic conditions divalent cations, such as calcium will hold together a matrix of LS micelles to form a gel. When this

calcium is removed, the spheres can disintegrate and reduce the molecular mass distribution dramatically.

For the study it was decided to hold the fouling conditions constant and vary only process parameters during cleaning. The factors investigated were those that have the biggest impact on cost, which are the type of cleaning agent (mono-or formulated composition), the concentration and the temperature of the solution. A formulated cleaning agent was chosen: *Ultrasil 11* from *Ecolab*, since it is known in industry as a good cleaner and is in widespread use. NaOH was also used, mainly because it is the major ingredient of *Ultrasil 11*, hence a comparison of performance with *Ultrasil 11* would reveal a lot information concerning the ingredients and their importance over different time sections during long term-cleaning. Since *Ultrasil 11* contains surfactants, which will almost certainly adsorb to the membrane surface, a brief literature review is given on the adsorption behaviour of surfactants on polymeric surfaces. The adsorption will depend upon the particular surfactant and upon the type of membrane. Major factors influencing the degree of adsorption are the solution temperature and the hydrophobicity of the membrane.

Chapter 3

Material

&

Methods

3 Introduction

The previous chapter dealt with the description of the separation problem and the difficulties industry is facing regarding the cleaning of membranes. This was leading to the formulation of the objects of study and the restriction the experimentalist is facing by proving a diversity of hypothesis. This chapter will deal with (i) experimental design and methods used for carrying out the filtration experiments, and (ii) analytical methods as zeta potential, ATR-FTIR and others.

With the exception of the mass analyses of SSL fractions, the analytical measurements were carried out at Lappeenranta University of Technology (LUT)/Finland. The laboratory of membrane science at LUT is lead by Prof. M. Nyström. It is a word-class laboratory and provided access to expensive equipment and expertise in handling a variety of complete different analytical techniques. Therefore, membrane samples had been prepared and then contained in pure water and stored in a fridge. Concern was raised that the stored membrane could age and alter the results. This issue will be dealt with in the result section.

3.1 The experimental set-up

A rig was set up in order to have enough capacity to create sufficient flow, pressure and heat for two flat sheet membrane modules in series. The following engineering concepts were tried to achieve:

- easy and fast operation
- flexibility
- delivery of reliable results
- robust and safe

Bartlett 1998 had designed an experimental rig which had separated pipes for the cleaning, rinsing and fouling solution in order to ensure the solutions from pollution with remaining (fouling-) material from the pipe walls. This concept was

abandoned, since Bartlett's rig still interfaced the pump and valves, which shared surfaces with all the processed solutions. In addition, spent sulphite liquor is not a material suitable for any kind of biological growth, unlike the whey protein solution used by *Bartlett* and other researchers. Therefore severe contamination from biomaterial could be ruled out. So, instead a straightforward experimental rig was designed to fulfil the stated design aims.

3.1.1 The cleaning and fouling rig

The materials for the rig are either plastic (PVC-Derivative) or stainless steel of type 316. The usage of this material is necessary, since wood pulp liquor is highly corrosive.

The cleaning and fouling rig is shown in figure 3.1. It can be fed with three different solutions. Three calibrated, polyethylene holding tanks of small size (50 litres), can hold the fouling solution, the cleaning solution and pure water for rinsing. The desired liquid is sucked by a six stage centrifugal pump from *Lovara* (Type:SV2-11T15M). The pipe-work and valves between tanks and pump are made of 1" (25,4 mm) UPVC from *Durapipe*^{TM}. The solution is then passed through a plate heat exchange to reach the desired temperature. With 9 plates an exchange area of 0.3 m^2 is achieved and the heat exchange is established with a counter-current of heat-transfer oil. The oil is pumped from an external Heater from „Conair" through the plates. After passing the heat exchanger, the liquid is divided to a bypass and the main pipe. The bypass returns a surplus of flow through a flexible hose back to the tank; the main pipe leads to the membrane module. Before the solution enters the module, it has to pass a needle valve for the regulation of flow, then a magnetic flow meter and finally a valve. The valve is fitted into the system to have the option for recycling the solution without passing the modules, for example during the heating process. Right after the module, the liquid has to pass a second needle valve, which is necessary to control the TMP over the modules. Finally the retentate is returned back to the tank. The rest of the tubing, which means all pipes and hoses after the pump are constructed of 0.5"(12, 27 mm) o.d. 316 stainless steel. Also the connectors and valves

(*Swagelok Ltd*) were of 316 stainless steel and rated to 10 bar pressure. The pump is capable of achieving flow rates up to 16L/min. Each process solution is recycled through the bypasses until the required flow and temperature are attained. Then the flow is redirected to the module, where the solution is separated by the membrane into retentate and permeates. Both are recycled into the feed tank, to maintain a constant feed concentration. The permeate line is made of a 0.25" stainless steel pipe and fitted with an On/Off valve. The permeate is collected in a beaker positioned on a balance. The change of weight is signalled to a computer, where software is translating the signal into the permeate output per time. A computer is used to monitor temperatures, pressures and feed and permeate flow. The software used is GENIE, Application builder for Data, Acquisition and Control, Version 3.0, ADVANTECH, Copyright 1993-95 American advantech corp.

To ensure that shared lines are not contaminated from the previous process solution, the complete line is drained, before taking new solution. For this, the bypass line and the return line from the retentate are constructed as flexible hoses. Both lines are placed for this purpose simply over the drain until the old solution is replaced, before switching to recycle in order to attain the desired flow and temperature conditions for the next run.

The shutdown of the system requires the complete removal of the process streams and can be done by opening a valve on the deepest point of the entire rig. All liquid is flowing then due to gravity to the drain. A drawing of the rig can be seen in Figure 3.1.

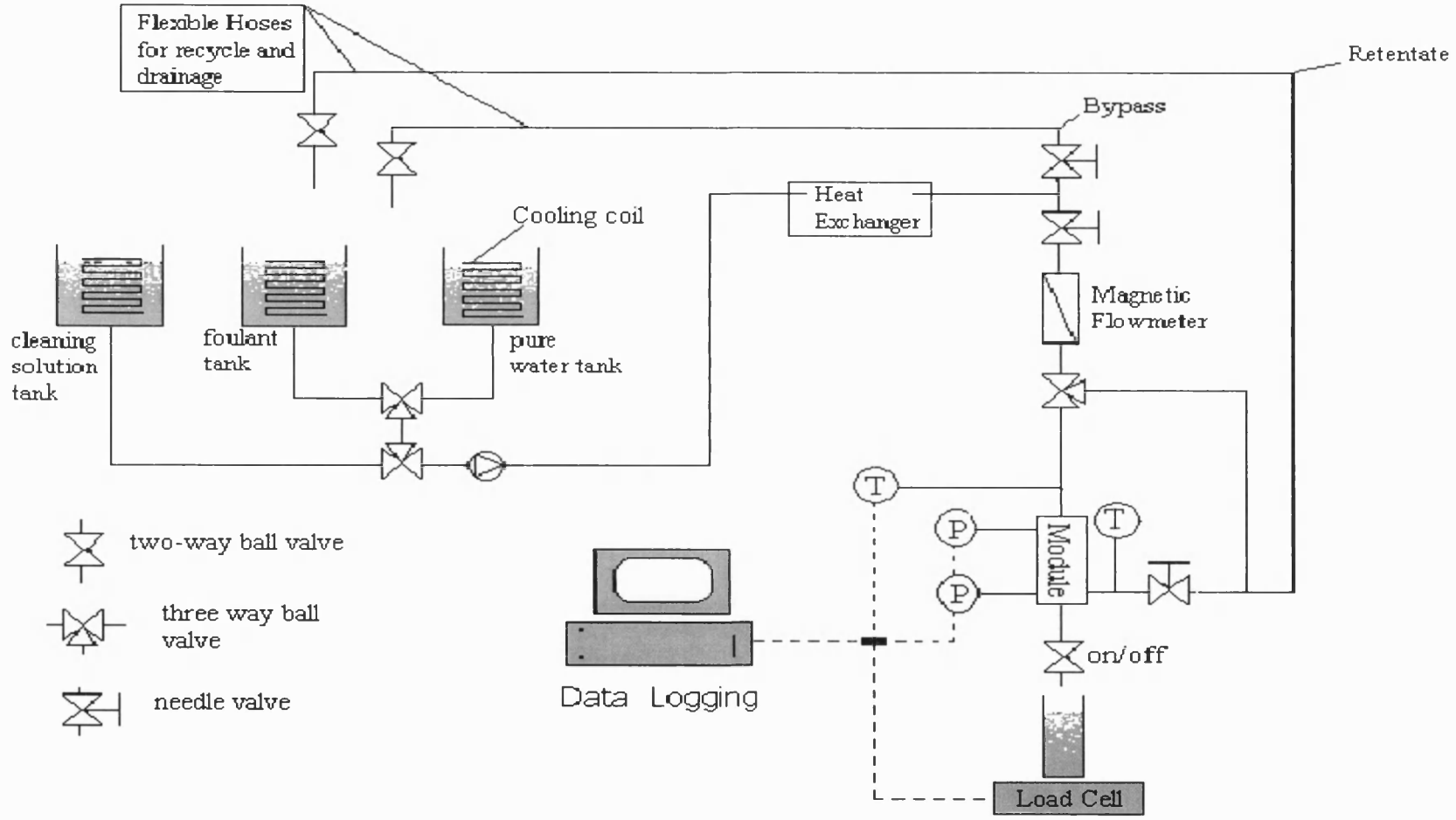


Figure 3.1: Schematic diagram of the fouling and cleaning rig used in this study

3.1.2 The modules

The selection criteria for the membrane module were the industrial relevance and accessibility of the membranes. A flat-sheet membrane module fulfilled these two criteria. As mentioned earlier these modules are used in Industries, since they are not as susceptible to fibre clogging as for example hollow fibre or spiral wound arrangements. Also for laboratory application and research, flat-sheet modules have the advantage that they can host any kind of membrane. Furthermore, they can be easily removed without damaging, which is vital for *ex situ* investigation such as scanning electron microscopy or streaming potential measurements.

A module made of High-density polyethylene, which was designed to house any flat-sheet membrane of 10 cm x 20 cm, is shown schematically in Figure 3.2. The module includes a double O-ring system to ensure sealing. An insert of polypropylene with pores of 1 μm is used to support the membrane test-section. This type of module was first introduced by *Aimar et al.* 1989 who validated the flow distribution between channels using a high speed video camera and a Perspex insert.

A replaceable Perspex insert allows for channel geometry, and hence CFV to be controlled. An insert providing 7 channels of 7 mm width, 1 mm height and 191 mm in length was used for this study, unless otherwise stated, to provide a filtration area of 95 cm^2. Sample calculations of the linear flow rate and Reynolds number for a given volumetric flow rate are given in Appendix.

The lid and base of the membrane module are sealed together with either eight bolts or clamps. A technical drawing of the top part of the module can be seen in Figure 3.3 and a drawing of the bottom part in Figure 3.4 respectively.

Figure 3.5 shows a detailed view of the channel insert for establishing a correct flow distribution and a desired shear-rate. The actual optimisation of the flow distribution proved to be very difficult. The flow distribution was adjusted using the approach from *Aimar*, by covering the top part of the module with a transparent Perspex sheet. At low flow rates, a strong dye was injected into the pipe system with a syringe just shortly before the module. The dye stained the

water and then the flow distribution could be easily observed with the naked eye. Since the distribution was not satisfactory at the first design stage, some modifications of the channel insert were done. In order to break the jet stream of the incoming solution and to allow a mixing prior before the solution is entering the channels, a mixing area was carved out of the entrance section of the channel insert. The exact dimensions of this "mixing area" can be found in Figure 3.5 in the cross section view of the channel insert. This area improved the flow distribution significantly. When doing filtration experiments it was found that fouling layers were evenly distributed over the whole membrane sheet. Therefore, the design was found to be satisfactory for the tasks lying ahead. It was decided to spend time and effort to design our own module, since it delivers scientifically reliable results. An alternative would have been to buy commercial available flat-sheet modules. Unfortunately these modules are not provided with detailed data concerning flow distribution and channel dimensions and therefore any adjustment of critical flow parameters, for instance shear rate, proves to be difficult.

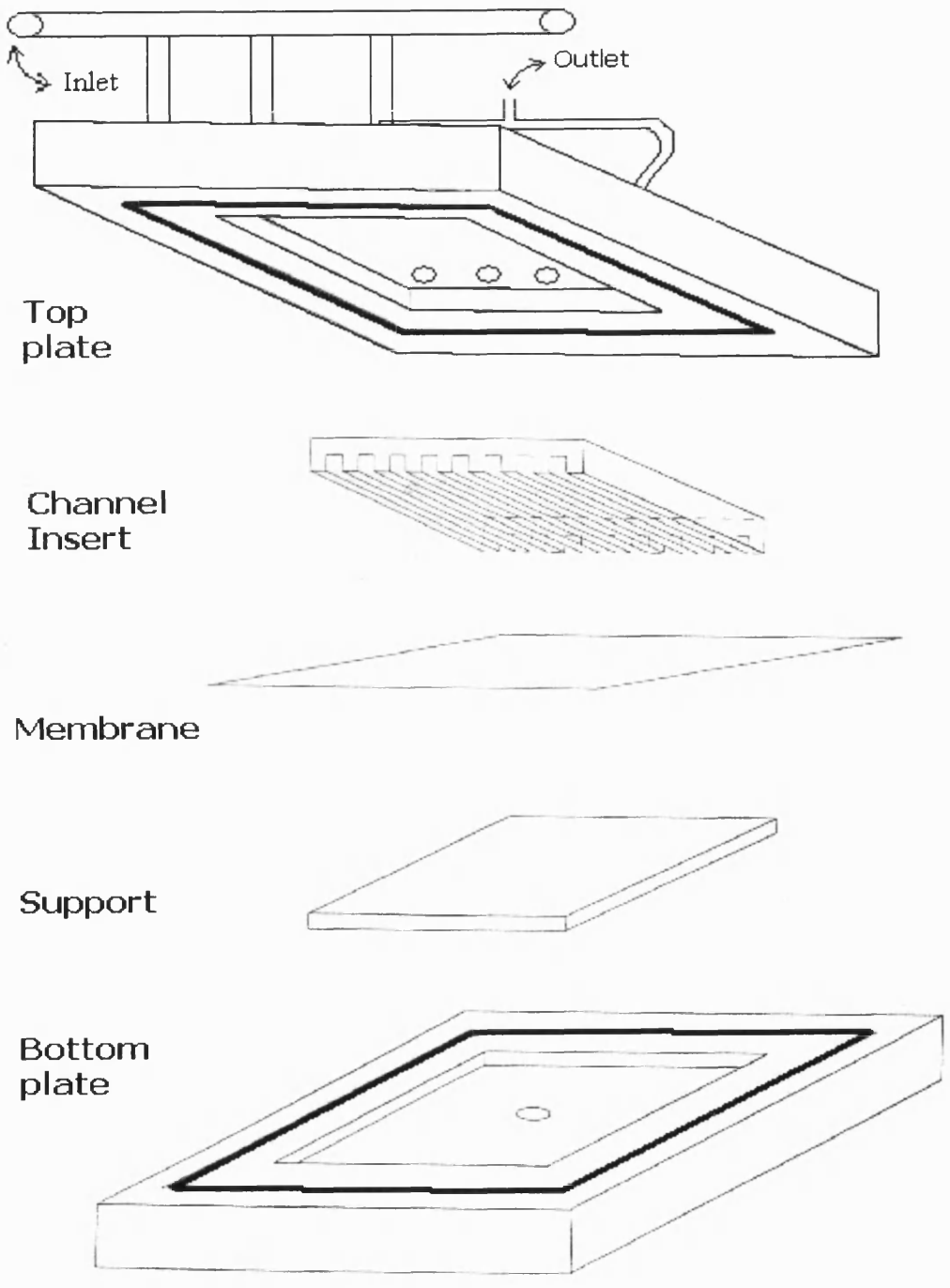


Figure 3.2: Schematic diagram of the module [After Bartlett 1992]

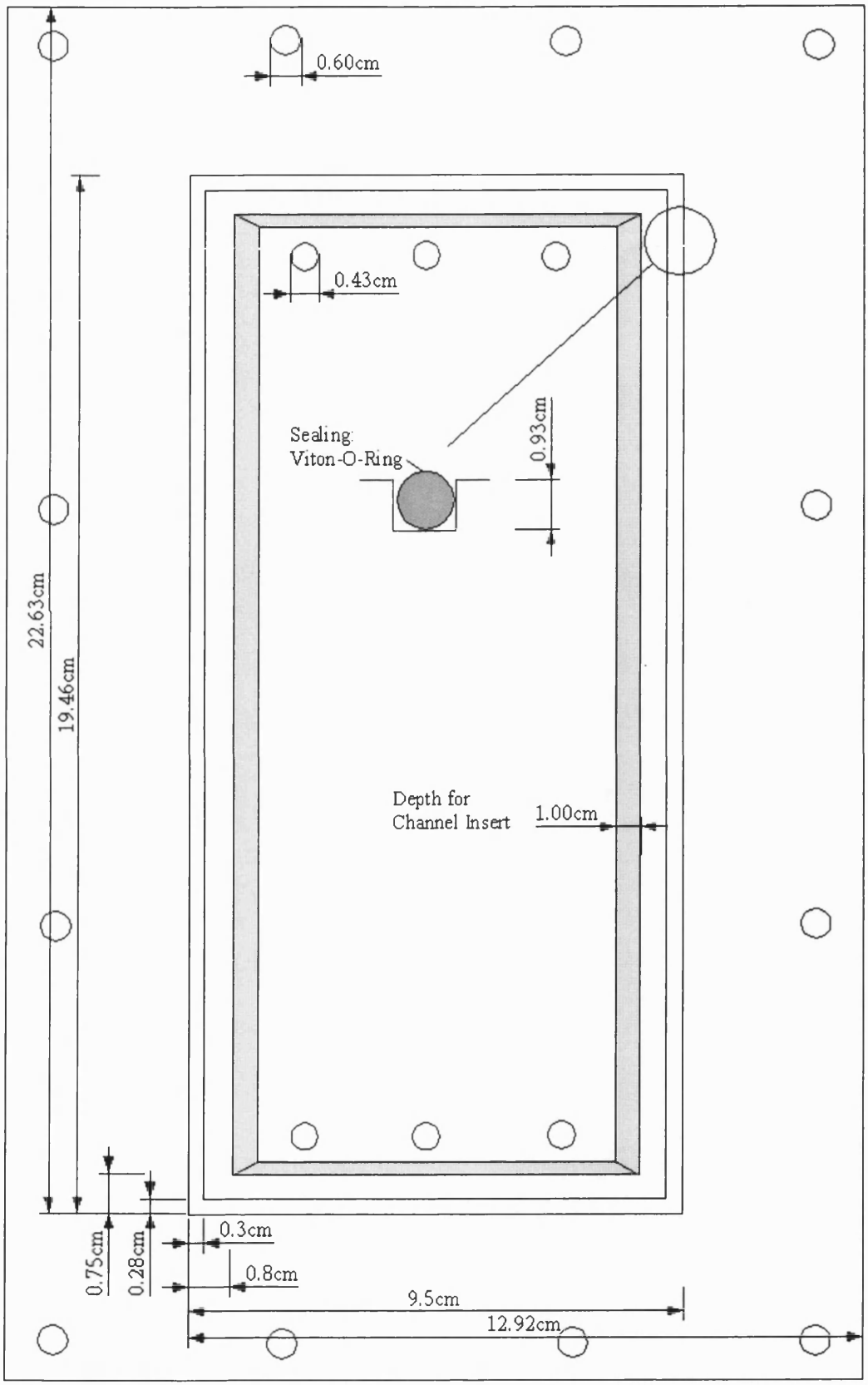


Figure 3.3: Module top part

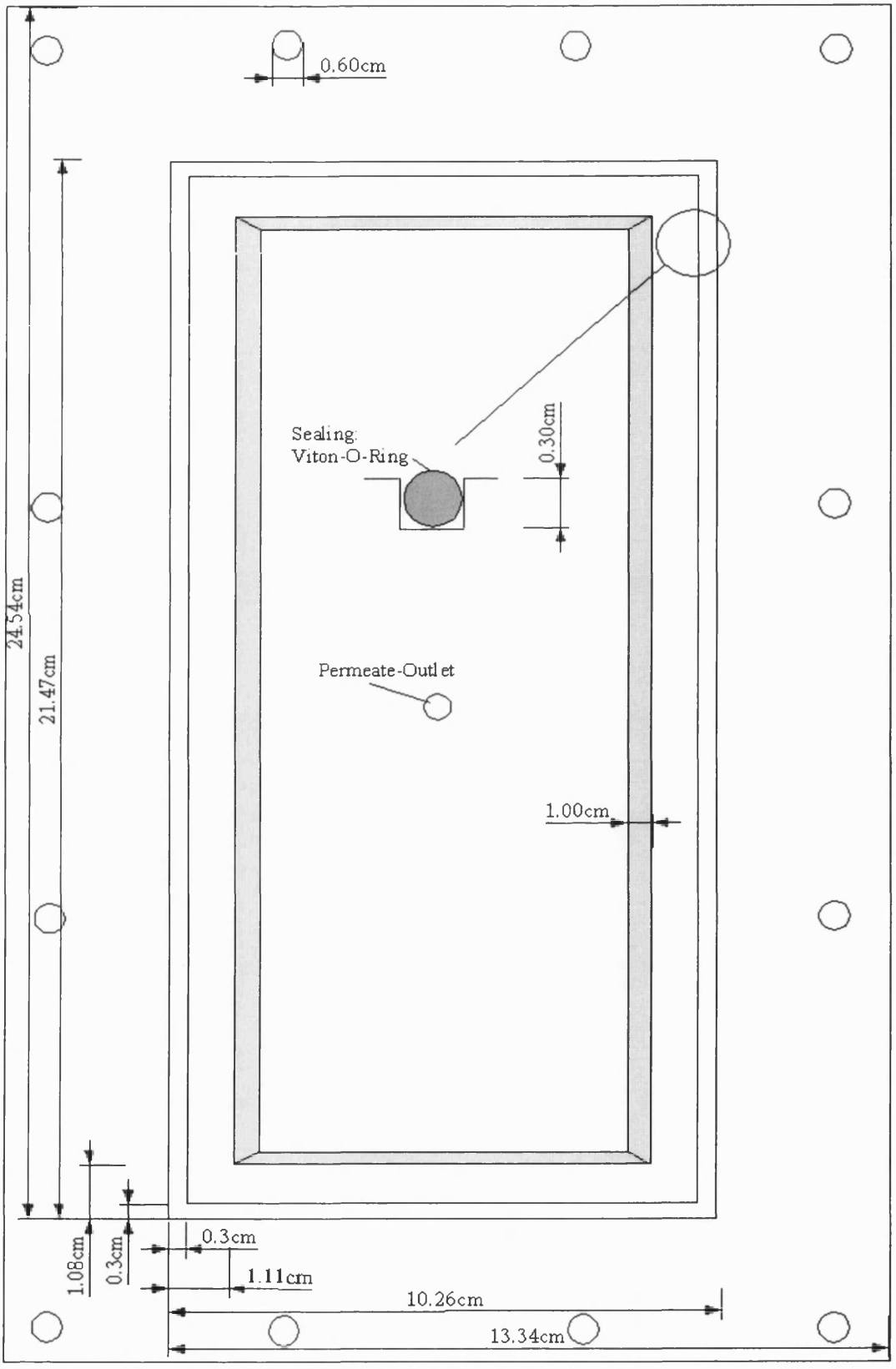


Figure 3.4: Module bottom part

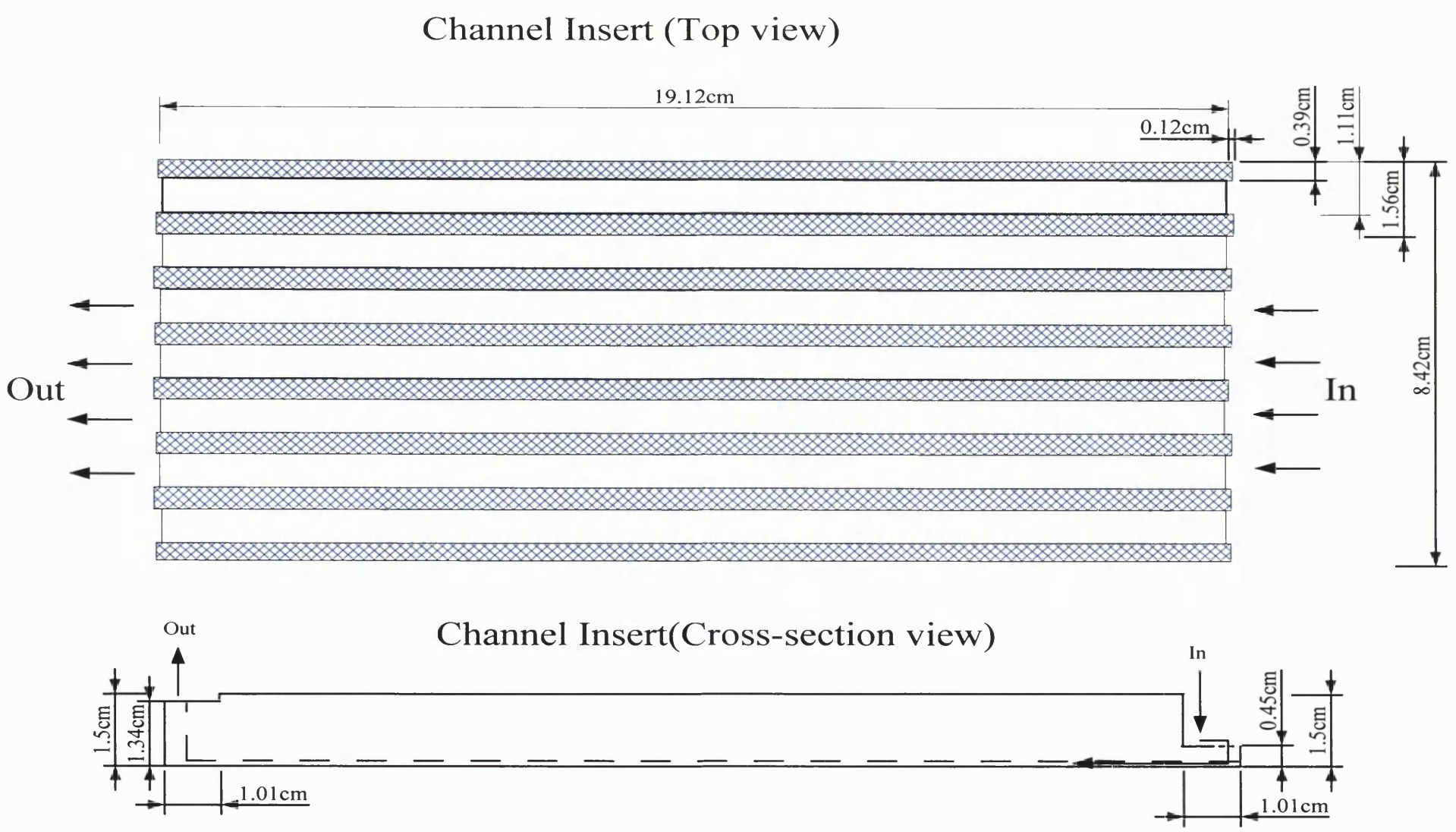


Figure 3.5: Channel insert; top - and cross-section view

3.1.3 The membranes

The membranes used for the study were Polyethersulphone (PES), Polysulphone (PSf) and regenerated Cellulose (RC). The choice followed three main criteria:

1. The usage and significance for industry (membrane price),
2. The costs for cleaning the membrane (the membrane material determines the cleaning regime, such as temperature and concentration of solution),
3. Different membrane hydrophobicity.

Bowen and Doneva 2000 pointed out that the morphology of the membrane will also influence the fouling behaviour. Therefore AFM pictures were obtained in order to acquire information about the surface roughness and area. This was done as part of a separate project by *Chukwuemeka* 2002. Nevertheless the pictures are displayed (Figures 3.7-3.9) together with a brief description of the used measuring principle of AFM.

3.1.4 Atomic Force Microscopy (AFM)

Atomic force microscope was introduced to measure extremely small forces up to $10^{-12} - 10^{-8}$ N, *Martin* et al. 1987 and *Burnham and Colton* 1989. It also provides a general method for doing non-destructive surface profilometry at a resolution better than 10 nm and perhaps down the atomic level. The signal for surface profiling comes from the variations in the force between the tip and the surface atoms. The advantages in comparison to other profiling methods are displayed in Table 3.1.

Table 3.1: Characteristics of various profiling methods

	Optical Microscopy	**Scanning electron microscopy**	**Atomic force microscopy**
Resolution: x,y	1.0μm	5.0μm	2-10nm for AFM 0.1nm for STM
Resolution: z	None	None	0.1nm for AFM 0.01 nm for STM
Effective Magnification	$1\times10^{3}\times$	$10\times$ - $10^{6}\times$	$5\times10^{2}\times$ - $10^{8}\times$
Sample preparation requirement	Little	Little to substantial	Little or none
Characteristics required of sample	Sample must not be completely transparent to light wavelength used	Surface must not build up charge and must be vacuum compatible	Sample must not have local variations in surface height >10μm.

The core element of an AFM is a cantilever (see Figure 3.6), with a tip at the end directed towards the sample. On top of the cantilever head a laser beam is reflected towards a photo detector, which consists of two side-by-side photodiodes, *Prater* et al. 2001. The magnitude of the angular reflection can be derived from the difference between the two photodiode signals detected by the photodiode detector. The "hills" and the "valleys" that constitute the topography of the surface can be resolved from the plot of laser reflection versus the tip position on the sample surface.

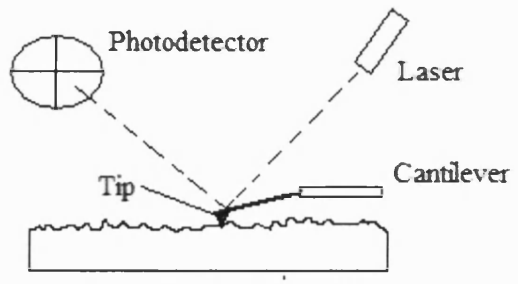


Figure 3.6: The core element of an AFM

In the so called contact mode, which was used in this study, the cantilever is scanned in a raster pattern along the surface of the sample. During the scan the tip of the cantilever is making permanent contact with the sample. The bending is caused by the attraction force of the sample (Van-der Waals forces) and is monitored by the laser reflection and the sensors. To enable the cantilever to follow hills and valleys of the sample and to avoid the cantilever getting stuck in the sample, the sensor is attached to a feedback loop, which moves the sample in vertical direction to the cantilever in oder to maintain a constant distance between sample and cantilever. The contact mode should not be used for soft material like polymers, since the dragging force can cause artefacts. To avoid such artefact, a variation is used, the Tapping Mode™. In this mode, the cantilever is oscillating with a high frequency just above the surface of the sample. The oscillation amplitude is set sufficiently high (10-100nm) that when the probe taps on the surface, the cantilever has sufficient restoring force to prevent the tip from getting trapped in the adsorbed fluid layer exerting electrostatic attraction with the sample and the tip. When the cantilever is coming closer to the surface the oscillating amplitude is reduced, which is monitored again by the sensors and used for topography mapping. The advantage of the tapping mode is that due to the oscillating the time of contact is reduced and the force exerted on the sample is only of negligible vertical nature and no lateral forces are present as with the contact mode. However, the contact mode offers higher resolution pictures and with some care taken, artefacts can be avoided. Therefore contact mode was chosen and data were obtained using the Multimode AFM (Nanoscope III, Digital Instruments, Santa Barabara, CA). As cantilever orobe was used a standard solicon nitride probe and had the following specifications:

Sprong or force constant:	0.32 N/m
Nominal tip radius of curvature:	20 nm
Cantilever configuration and length:	V-shaped / 200 μm
Reflective coating and shape of tip:	Gold / Square pyramidal
Tip half angle:	35 °

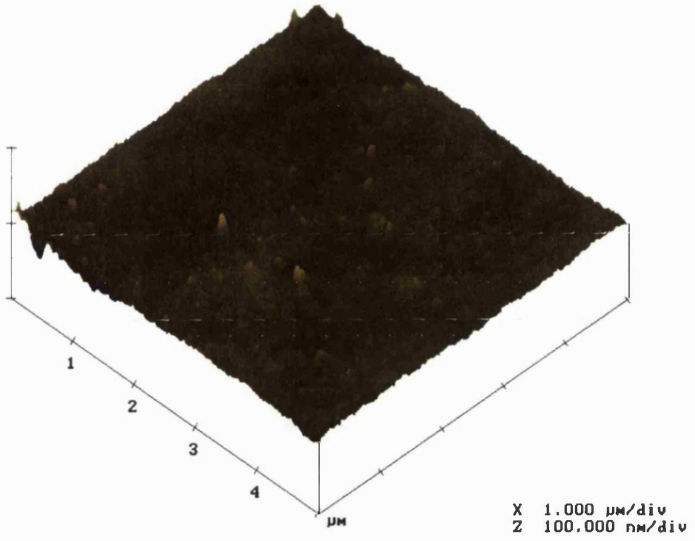


Figure 3.7: Virgin RC membrane

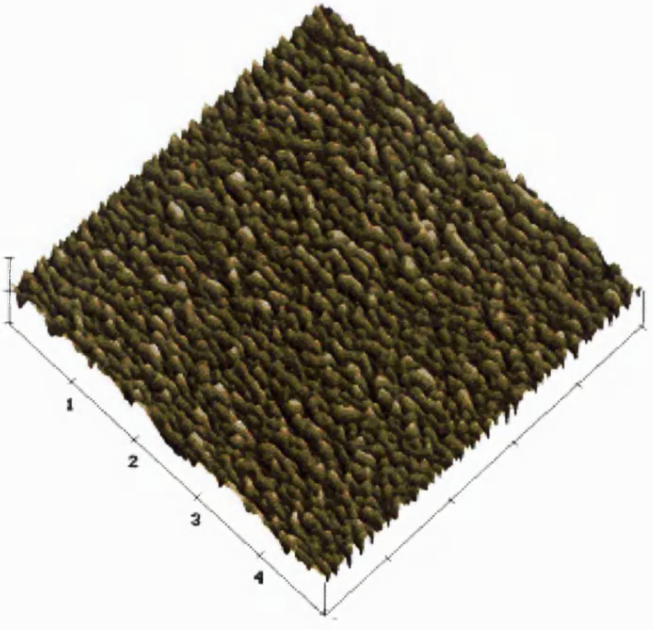


Figure 3.8: Virgin PES membrane

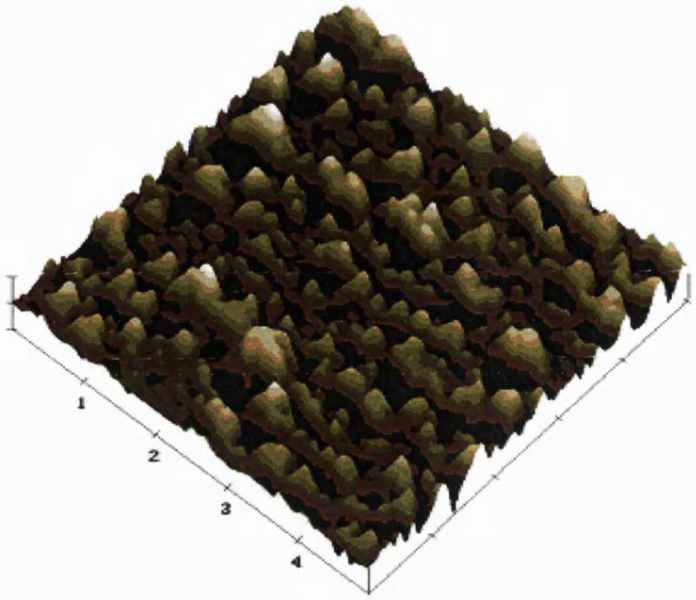


Figure 3.9: Virgin PSf membrane

As can be easily seen in the pictures the roughness is the lowest for the RC membrane and the highest for the PSf membrane. The surface area was calculated for 5 μm^2 on all three membranes and was found the highest for PES, then PSf and finally RC with the lowest surface area. The implication of roughness and area per surface unit will be discussed in the result chapter.

3.1.5 The cleaning and fouling procedures (protocol)

When doing filtration experiments, in particular when carrying out cleaning tests, a standardised method of operation is essential for success. When developing such a protocol, the experimentalist is restricted by some necessities, which need to be carried out to ensure secure results. Among those restrictions is the permanent rinsing between each cleaning and fouling cycle. Also, the use of pure water, standardised to a certain pH is essential to make results comparable. In reality that is different and it should be mentioned that industrial practise of rinsing pipes, tanks and modules is carried out with simple tap water containing metal cations and a changing pH.

Also, before a virgin membrane can be tested for the pure water flux (an important parameter of performance) the membrane needs to be pressurised under the actual

operation pressure until a stable water flux is established. Furthermore, commercial membranes are coated with glycerine, a preservative to ensure that the remains wetted. If the membrane dries out this will produce cracks in the sensitive thin top layer, so that such a membrane cannot be used any more. Theoretically, this glycerine is highly water-soluble and therefore thought to be easily removed by rinsing the membrane with pure water. In practice that proved absolutely not to be the case and caused major problems. A section in the chapter "results" will therefore be devoted to the problem of glycerine removal. In fact, in a literature review it was found that there is no standardised method for the removal of glycerine and researchers are simply not aware that glycerine could change membrane performance. In this study, a method was developed to remove glycerine to a sufficient degree. The degree of removal was checked with TOC measurement. Once, the TOC values were that of pure water, rinsing of the membrane was stopped and used for further experiments.

The pressurising and the removal of glycerine are summarised in the term "conditioning". Both procedures should be carried out to ensure the real performance of the membrane is established before measuring the pure water flux **(PWF)** of the membrane. After that is done fouling and cleaning cycles will follow. The term **"cycle"** should be defined since it will be used in this study on a frequent basis. One cycle comprises the following steps:

1. **fouling step:** the actual separation of the feed is carried out into retentate and permeate
2. **PWF-measurements:** the measurements will determine the effect of irreversible fouling.
3. **Rinsing:** the membrane is rinsed with pure water at a certain temperature and period of time to remove loose deposits.
4. **PWF-measurements**: the measurements will determine the effect of rinsing
5. **Cleaning:** the membrane is cleaned with a cleaning solution at a certain temperature and period of time.

6. **Inter-Rinsing:** the membrane is rinsed again to ensure remaining cleaner is flushed from the membrane and system. This is done until a stable flux and pH value is achieved.
7. **PWF-measurements:** the measurements will determine the effect of cleaning.

Basically two different kinds of protocols were developed. These protocols are following the common practise in the dairy industry (*Renner and Abd El-Salam* 1991) and in the pulp and paper industry (*Blackwell et al.* 1992, *Wallberg et al.* 2001), with rinsing to remove loose deposits and chemical cleaning afterwards. In particular protocol 2 is very close to industrial practise, but in general one should be aware of the fact that the final procedures practised in industry depend on the particular membrane used, the feed material, type of module and various process parameters. Therefore, all the parameters for the protocols might differ in reality. In protocol 1 the ambient cleaning temperature, is unusual and would not be used in industry. Nevertheless it is very helpful to understand the function of cleaning agent ingredients and the role of temperature over long time. The process parameters used in both steps are written down in Table 3.2, but the main differences are as follows:

- The **first protocol** compromises a conditioning step insufficient for the removal of glycerine and a formulated cleaning agent is used, *Ultrasil 11*. Both will most likely change the membrane surface in hydrophobicity and charge and affect the short and long term performance. Also, the cleaning is carried out at ambient temperatures, which also has a significant impact on the performance.
- The **second protocol** is basically the opposite of the first protocol. A sufficient conditioning process with pure water was used to remove glycerine and no cleaning agent was used during the conditioning. Also, the temperature was much higher for the cleaning step.

The carrying out of both protocols will show the impact of the relevant things to do when considering membrane filtration.

As mentioned, the removal of glycerine is generally one step of "conditioning". An additional step of pressurising the membrane under the conditions found during the actual separation (fouling) step was found not to be necessary, since pressurising the membrane did not lead to any flux decline and the flux was proportional to the increase in pressure.

The parameters within a "cycle" are slightly different between the 1st and the 2nd protocol, in particular the parameter pressure. This might affect the absolute results within a cycle, but not the trend over many cycles. Therefore, trends over more than one cycle can still be compared and conclusions are drawn.

For the regenerated cellulose membrane, entirely different process conditions had to be chosen for the fouling and cleaning step. This was mainly because the material can withstand less severe conditions than for instance PES or PSf. Experiments were still carried out, since regenerate cellulose is of great interest, because it is cheap and extremely hydrophilic. **For the full protocols, please see Appendix 7.2.**

Table 3.2: Protocols used for fouling and cleaning experiments (for PES from Nadir)

	1st protocol "Cold wash"	2nd protocol "Hot wash"
removal of glycerine: (conditioning)	at 22°C, 30 min., 1.5 bar, 1.8 ms^{-1} with 0.1 wt% Ultrasil 11 – solution	at 60°C, 90 min., 1.0 bar, 1.8 ms^{-1} with pure water.
PWF measurements	at 22°C, 5.25 bar, CFV 2.7 ms^{-1}	at 22°C, 1,00 bar, CFV 2.7 ms^{-1}
Fouling	at 70°C 8.25 bar, CFV 2.7 ms^{-1} for 90 min.	at 70°C 7.00 bar, CFV 2.7 ms^{-1} for 120 min.
1 PWF after fouling	Not measured	at 22°C, 1,00 bar, CFV 2.7 ms^{-1}
Rinsing	at 22°C, 1.5 bar, CFV 1.8 ms^{-1} for 15 min.	at 22°C, 1,00 bar, CFV 2.7 ms^{-1} for 15 min.
2.PWF after rinsing	Not measured	at 22°C, 1,00 bar, CFV 2.7 ms^{-1}
Cleaning	at 22°C, 1.5 bar, CFV 1.8 ms^{-1}, for 30 min with 0.5 wt% NaOH or Ultrasil 11 solution	at 60°C, 1.0 bar, CFV 1.8 ms^{-1}, for 30 min with 0.5 wt% NaOH or Ultrasil 11 solution
Inter-rinsing	at 22°C, 1.5 bar, CFV 1.8 ms^{-1} until pH and flux constant.	at 22°C, 1.0 bar, CFV 1.8 ms^{-1} until pH and flux constant.
3.PWF after cleaning	at 22°C, 5.25 bar, CFV 2.7 ms^{-1}	at 22°C, 1,00 bar, CFV 2.7 ms^{-1}

3.1.6 The choice of operation parameters

Some operational parameters are fixed, since they are not of direct importance for the outcome of the study. But the choice of these parameters has still some significance for the overall meaning of the results.

Fouling

- time: the impact of the duration of the actual separation on the degree of fouling was investigated for both protocols and can be seen in the results. As expected due to the gel layer effect, a quasi steady state was established after 1.5 hours of filtration. The gel layer becomes the dominant limiting separation factor and after that only a negligible decline can be observed even after 24 hours. Due to constrains of the research project, like limited time, it was decided to stop the fouling step after that steady state was reached, since a further decline is rather small. In industry the cleaning frequency varies between 1 day and 1 week. For the second protocol it was decided to extend the fouling time for a further ½ hour, in order to ensure to pass the point where the steady-state was first established.
- temperature: the temperature for the PES and PSf was 70°C as used in industry (*Wallberg* 2001).
- pressure: high TMP led to a more rapid flux decline and a lower stable flux level as the consequence of a more compact cake formation and greater in-pore fouling. (*Gan et al.* 1997). For the sake of economical fluxes, industry works at around 7 bar, which will be used in this study as well.
- flow velocity: turbulent flow as used in industry. Crossflow is effective in reducing concentration polarisation at the membrane surface. The total quantity of deposits and their stability within the stagnant boundary layer of the fluid is known to be dependant on the crossflow velocity and fluid turbulence patterns. (*Gan et al.* 1999).

Rinsing

- time: rinsing was set to 15 minute removal of loose material occurred within the first 10 min. It represents an industrial standard.
- pressure and flow velocity: In order to enhance removal of loose deposits turbulent conditions were used. It was decided to operate under 1 bar

pressure, since the pores should also get flushed. (*Nakanishi and Kessler* 1985)

Cleaning

- time: experiments showed that 30 minute was a sufficient time, within 90 percent of the flux recovery occurring in the first 10 min of the total cleaning time.
- pressure and flow velocity: In order to enhance removal of loose deposit turbulent conditions were used. It was decided to operate under 1 bar pressure, since the pores should also get flushed. It represents an industrial standard.

3.2 The zeta potential measurements

The surface properties (e.g. charge) on a synthetic virgin membrane have a significant influence upon its separation properties and fouling tendencies, (*Hvid et al.* 1990 and *Ulbricht and Belfort* 1996) to name only a few. It is assumed that the same is valid for fouled or cleaned membranes. The surface charge density of a porous membrane is related to the zeta potential of the membrane.

The presence of a surface charge leads to ions in the solution of an opposite charge being attracted towards the surface. This leads to a greater concentration of counter ions close to the surface than in the bulk of the liquid, a concentration that falls off with increasing distance from the surface. One should be aware that when a neutral surface is exposed to an ionic solution, a difference in affinity of hydrated ions for the surface can cause one type (charge) of ion to become more closely associated with the surface. There is a bound layer of counter-ions (called the Stern layer) at the surface and followed by a more diffuse layer at greater distances from the surface. The thickness of this "Stern layer" depends on the radius on the specifically adsorbed counter-ions. Beyond this layer is a more diffusive layer of counter-ions and co-ions (the same charge as the membrane surface). There is a plane of shear between the bound layer and the diffusive layer and the potential difference between the plane of shear and the bulk solution is

called the zeta-potential, which can be determined by measurements of electro-osmosis or streaming potential (*Elimelech et al.* 1995, *Hunter* 1996 and *Hiemenz* 1997). See also Figure 3.10.

A streaming potential arises when a pressure difference is applied across a membrane, causing the double layer to shear due to the flow of fluid which displaces the electric charge of the diffusive part of the double layer. This generates a potential in the opposite direction to the movement of the charges, which inhibits further dislocation of ions to achieve a steady state which is characterised by a stable potential difference called the **streaming potential.** It should be noted that the zeta-potential resembles the potential at the plane of shear and the adsorbed layer of counter ions and is not a direct measurement of the membrane surface potential, *Lyklema* 1985.

With the streaming potential, the **zeta potential (ζ)** can be calculated with the help of the Helmholtz-Smoluchowski equation.

$$\zeta = \frac{\Delta E}{\Delta p} \cdot \frac{\eta \kappa}{\varepsilon_o \varepsilon_r} \qquad (9)$$

where E is the streaming potential, p the pressure, η is the viscosity of the solvent, κ the conductivity of the electrolyte in the pores (approximated as bulk conductivity), ε_0 the permittivity of a vacuum, and ε_r the relative dielectric constant of the electrolyte.

In calculating zeta potentials (ζ) from streaming potential versus pressure (ΔE/Δp) measurements, the *Helmholtz-Smoluchowski* 1905 equation was used without corrections.

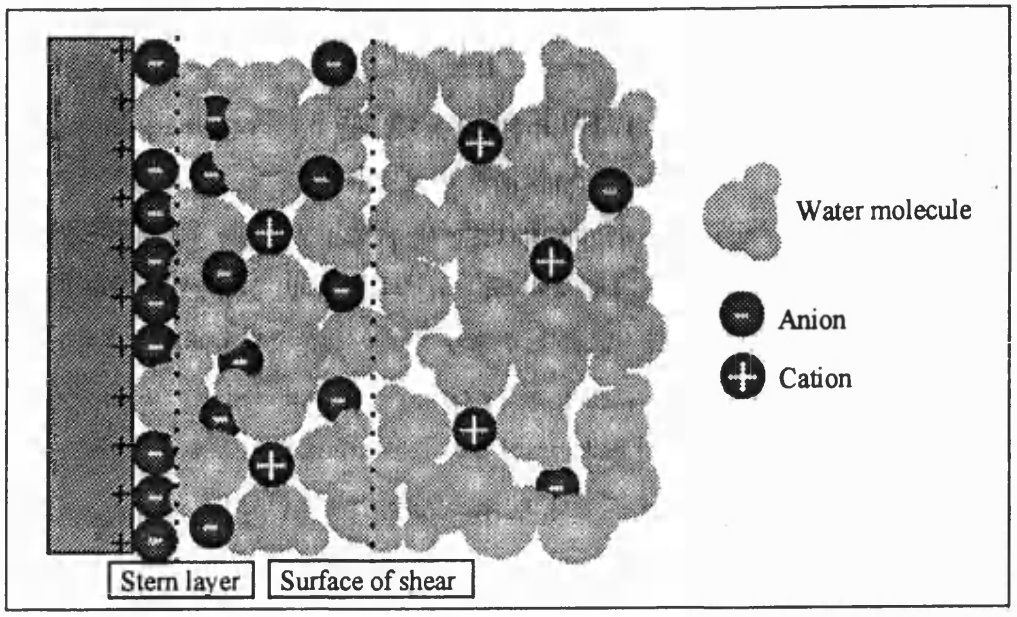


Figure 3.10: The electrical double layer according to the Gouy-Stern model

3.2.1 Problems with the prediction of zeta-potential from streaming potential measurements [Adapted from *Pihlajamäki* 1998]

Zeta-potential values of surfaces cannot be measured directly. What can be measured are other electrokinetic phenomena like the streaming potential described above. This is a rather straightforward procedure. However, the transformation from streaming-potential into zeta-potential with the equation above gives rise to some problems.

The biggest problem is the overlapping of the electrical double layer (EDL). In small pores the EDL will overlap and hence causing false results when applying pressure and determine the streaming potential. The broader the pore size distribution, the bigger the error. Pore forms (tortuosity and ionic strength of the solution) will add to the error range. A second problem is the surface conductance. Every surface will vary with roughness and that will affect the conductance. Many researchers have studied this problem intensively, but so far no model has been introduced to account for this phenomenon.

The correction of calculated apparent zeta-potential results after the Helmholtz-Smoluchowski equation is troublesome. So far, there are a few mathematical

models available to account for different problems. The most complete and correct model is still subject of academic debate. Also, when using correction factors some physical parameters need to be known, such as the pore size distribution. Since the pore size shrinks with continuing fouling and cleaning cycles and therefore affects the streaming potential, it is useless to try to apply corrections. Therefore it was decided to use the apparent zeta-potential values. The aim of obtaining the zeta-potential was to see the effect of cleaning upon the fouling and vice-versa. This could still be done with just the apparent value without sacrificing the scientific value of those results. What is desired is the degree of change, but not necessarily the absolute "true" value of the zeta-potentials. Also, the zeta-potential can not be used solely to draw conclusions. Only when combined together with other analytical methods can a complete picture be accomplished.

Beside the theoretical side there are also problems with the experimental procedure of measuring zeta-potential, which can result in large standard deviations, which are mainly assigned to membrane sample variability, *Keesom et al.* 1988. *Wilbert et al.* 1999 found that in addition to the sample variation the kinetics of equilibration between the electrolyte solution, the electrodes and the membrane has the greatest impact on measurement uncertainty. Therefore, great care was taken with stabilisation and a measurement was only started when only insignificant small changes in streaming potential were detected.

3.2.2 The zeta-potential apparatus and modules [After *Pihlajamäki* 1998]

In Figure 3.11 the streaming potential apparatus is presented. This apparatus can perform the streaming potential and flux measurements simultaneously. The data from the apparatus was collected in a file in a microcomputer by data acquisition software programmed with MS quickBASIC version 4.5 and using an ADDA 14-interface card. QuickBASIC was ideal for this kind of computing as it allowed easy and fast reprogramming. The streaming potential results were then moved to MS Excel 5.0 by reading the files from the diskette thus preventing the occurrence

of any typing errors. A template constructed in the Excel program calculated the zeta-potentials.

The module used is depicted in Figure 3.12 and is specially designed for measuring the zeta-potential through the pores. It can contain a membrane with an area of 10.2 cm^2. The electrodes are made of silver and the module of polycarbonate.

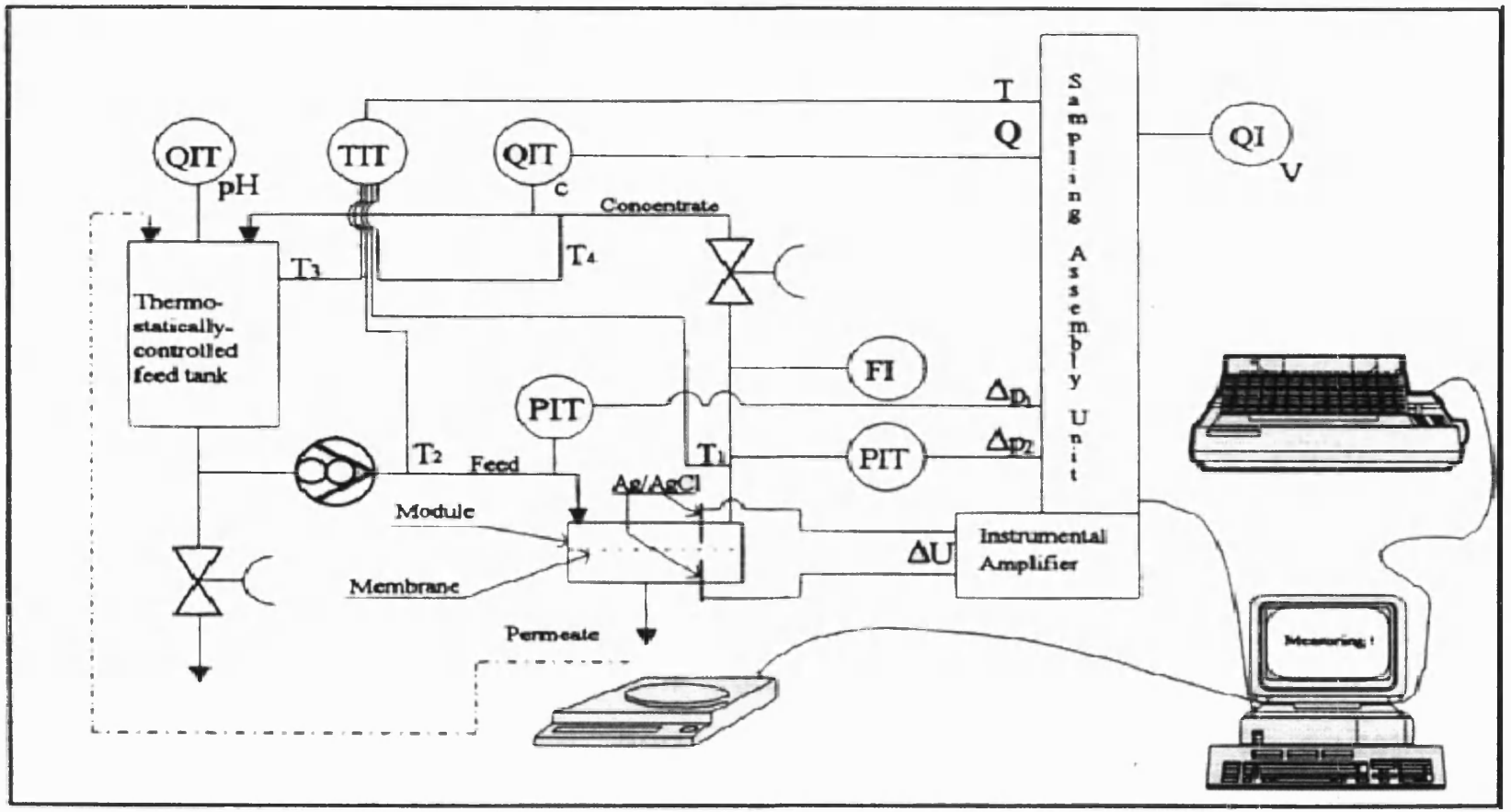


Figure 3.11: The streaming-potential apparatus [According to Pihlajamäki 1998]

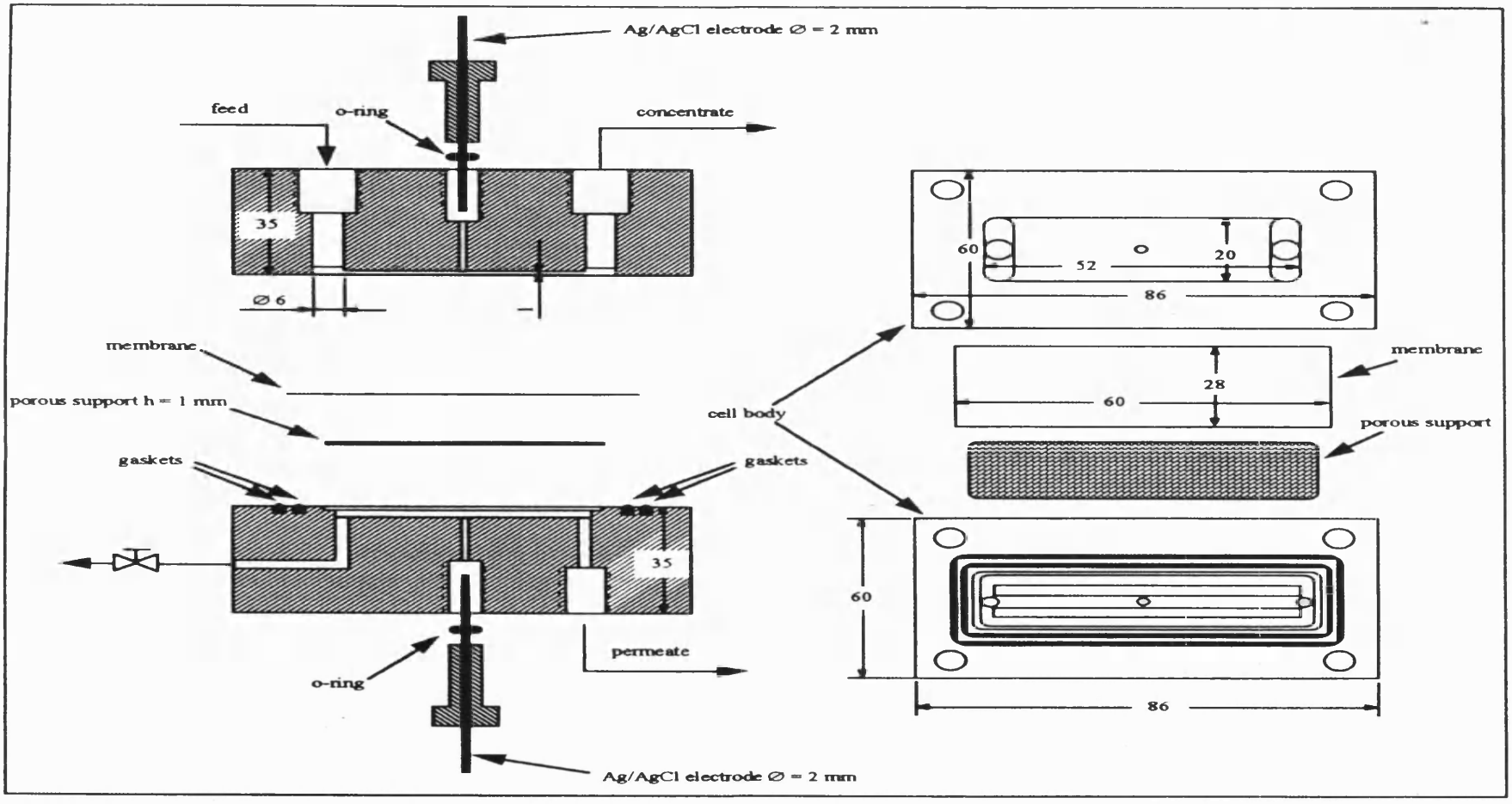


Figure 3.12: Module for the measurements of streaming potential through the pores of flat sheet membranes of area approximately 10.4 cm^2. Values in mm. [According to Pihlajamäki 1998]

3.3 The FTIR spectroscopy

Like photometry, the infrared spectroscopy works by the interaction of electromagnetic waves and matter. With the help of IR waves, the molecules in the specimen start to vibrate. This vibration starts if the energy of the infrared beam is as high as the energy of the basic vibration of the molecules. This is called the condition of resonance: the frequency of the infrared waves = the frequency of the molecule vibration. If the frequency of the infrared waves is higher than the frequency of the molecule vibration, adsorption of light takes place. The frequency of the adsorbed light and thus the frequency of the molecules in the sample can then be determined from the IR spectra. Since it is known at which frequency certain bonds and functional groups start to absorb, the exact structure of a studied substance can be determined by putting these single groups and bonds together to obtain the whole picture. (*Mattissek et al.* 1992).

3.3.1 ATR-FTIR spectroscopy

Simple IR spectroscopy can only be used for membranes if the IR waves are able to penetrate and pass through the membrane polymers. This is in most cases only possible if the thin skin layer can be peeled off from the support layer and if the membrane is not opaque. Otherwise, it is more convenient to use the ATR (attenuated total reflection) method to carry out surface analyses.

In this method the infrared beam is directed through a highly refractive crystal, which does not absorb in the infrared region. The IR light cannot leave the crystal, when the light has the right angle of incidence and the crystal the right refractive index. The radiation undergoes what is called **total internal reflection**. The infrared energy reflects off the crystal surface rather than leaving the crystal. By doing so, the IR beam reflects several time and travels through the whole crystal creating a standing wave of reflections, which is called an **evanescent wave.** A unique feature of the evanescent wave is that it is slightly bigger than the crystal, and so it penetrates a small distance beyond the crystal surface into space. The

membrane, or other solid material, is pressed against the crystal, the active layer facing the crystal surface. With each reflection, certain wavelengths are absorbed by the sample. That means the evanescent wave is attenuated by the sample's absorbance, hence the name **attenuated total reflectance**. A schematic diagram of the pathway through the crystal is shown is Figure 3.13.

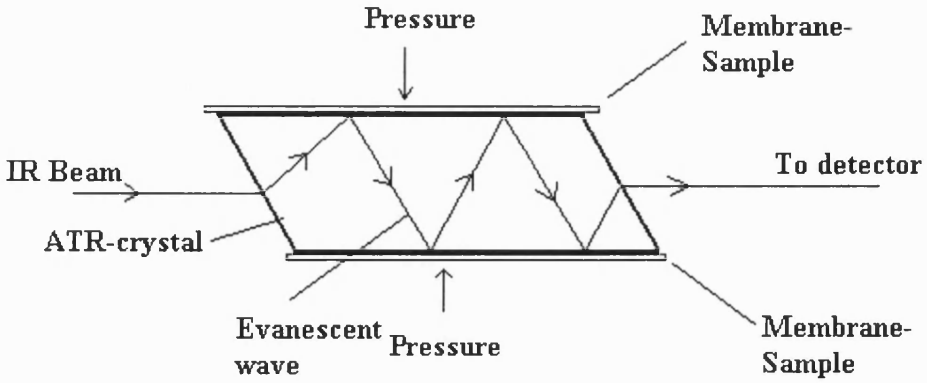


Figure 3.13: A schematic diagram of an attenuated total reflectance accessory.

How deeply the infrared beam penetrates into the sample, in this case the membrane; is known as the penetration depth, d_p, being given by equation (10).

$$d_p = \frac{\frac{\lambda}{n_1}}{2\pi\left[\sin^2\alpha\left(\frac{n_2}{n_1}\right)^2\right]^{1/2}} \qquad (10)$$

where λ is the infrared wavelength, n_1 and n_2 the refractive indices of the crystal and sample respectively, and α is the angle of incidence.

Depending on the properties of the membrane material, radiation is absorbed in the sample at certain wavelengths, which results in an attenuated signal at the infrared detector.

3.3.2 Problems with the interpretation of FTIR spectra and limitations

The penetration depth, depending on the angle of incidence, is rather large (0.1 to 5 micrometers is typical). Therefore it can sometimes be difficult to analyse a thin adsorbed layer. This problem can also be seen when studying the FTIR spectra presented in the result section of this thesis. Fouled and cleaned membrane spectra greatly resemble those of the pristine membrane and show only small changes. However, results still provide a good complement to other surface analysis methods. Another problem arises when infrared spectrometry is performed on substances comprising more than one typical bond or functional group, like polymers of membranes. Then many spectra contain peaks, which overlap with other peaks and produce a rather confusing picture. Also, some bonds and functional groups absorb at the same frequency. If a substance contains these particular structures it will leave peaks with double meanings or even more possible ways of interpretations. This makes the FTIR spectra difficult to use, even for trained analysts. Results should be handled with caution and only very significant appearances should be taken for any conclusions. A general limitation of infrared spectroscopy is that it cannot detect atoms or ions. Single atomic entities contain no chemical bonds, do not possess vibrational motion, and hence do not absorb infrared radiation.

3.3.3 The FTIR method used

A Perkin-Elmer 2000 FTIR apparatus was used in this study. It was provided with a HeNe laser as a radiation source (unpolarised IR radiation), triglycerine sulphate (TGS) as a detector and optical KBr as a beam splitter. The resolution of the FTIR apparatus was adjusted to 2.0 cm^{-1}, the optical path difference (OPD) velocity to 0.2 cm^{-1} and the data-collecting interval to 1.0. A KRS-5 crystal (thallium bromide iodide) was used as an internal reflection element (45°, 17 reflections). Every spectrum was made of 100 co-added scans, (*Pihlajamäki* 1998). Possible functional groups and bonds from peaks were determined with the help of the

Perkin-Elmer search program and reference books (*Hummel* [1978 and 1984] and *Socrates* 1994).

3.3.4 Proper use of manipulations

The manipulation of spectra is performed using the software that comes with an FTIR spectrometer, and involves altering or performing a calculation on the original spectrum received from the instrument. The purpose of manipulating a spectrum is to enhance its appearance, or extract more information from it. If spectral manipulations are not performed properly they can add artefacts to a spectrum, or completely destroy the integrity of the data. To avoid this problem, the analyst needs to put down the practice of manipulation exactly.

Blank

CO_2 and remaining moisture can produce peaks, which should not be there. These peaks can be removed by just deleting them. These peaks are easy to spot, since they always appear at the same wavelength.

Baseline Correction

Baseline corrections are used to correct spectra that have sloping or curved baselines, so the result is a flat baseline.

Smoothing

Smoothing is used on noisy spectra to reduce the noise level, so features that may have been hidden under the noise can be seen more readily. Thus, smoothing enhances the information content of the spectra. Smoothing has also a cosmetic effect, improving the overall appearance of poor looking data.

Normalize

The process of dividing all the absorbance values in a spectrum by the largest absorbance value. This resets the Y axis scale from 0 to 1 and makes spectra easier to compare.

3.4 Contact angle measurement

Information about wettability and therefore correlated properties such as surface free energy can be obtained by contact angle measurements. Surface free energy has been shown to affect bacterial adhesion, protein adsorption and effects of detergents on adsorbed proteins, *Zhang et al.* 1989. For the contact-angle measurements the sessil drop method was used. A drop of pure water is placed with a syringe on a porous membrane surface and the contact angle θ is measured as depicted in Figure 3.14. This is repeated 10 times, with measurements taken from both sides of the drop. The procedure is then repeated on another spot of the membrane. The total number of 40 angles is then averaged. To avoid drop volume changes due to evaporation or absorption, the time between the deposition of a drop and the measurement of the contact angles was kept as small as possible. For low affinity, in other words high hydrophobicity, the contact angle will have a value greater than 90°, whereas with high affinity (great hydrophilicity), the contact angle will be less than 90° tending even towards zero.

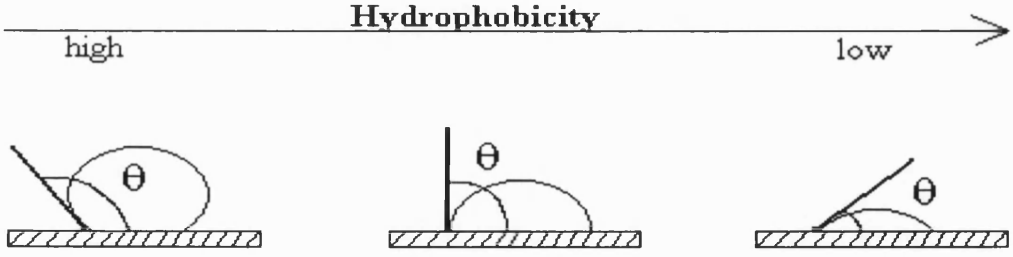


Figure 3.14: Contacts angles of liquid droplets on a solid, for instance membrane material

The contact angle will depend on

- pore size (r)
- surface tension of the liquid (β)
- surface energy of the membrane material (θ)

and can be described with the Laplace equation:

$$\cos\theta = \frac{r}{2\beta} x\Delta p \qquad (11)$$

If pressure p is applied, according to the Laplace equation, the liquid will penetrate into the membrane. In this study no pressure was applied and the remaining influencing parameters are the type of liquid and pore size. Therefore, it needs to be stated what liquid was used and the pore size. In this study pure water was used, which was and membranes with a molar mass cut-off of 30kD. Only the membrane material varied and with it the surface energy. Wetting is favoured when the solid polymer has a high surface energy.

3.4.1 Problems with measuring contact-angles

Contact angle measurements works well on hard surfaces, but on membranes with pores the results are distorted, due to hysteresis effects, *Kwok and Neuman* 1999. *Grundke et al.* 1996 noted that on rough and heterogeneous surfaces which exhibit contact angle hysteresis, contact angles can take any value between the maximum (advancing) and minimum (receding) contact angles. Even if membranes are from the same manufacturer and have the same molar mass cut-off, it is likely that they have slightly different surface roughness and pore size distribution. Both will influence the results and it should be taken into consideration when comparing acquired data from contact angle measurements. It becomes a problem in particular when small changes are detected, e.g. for fouled and cleaned membranes. Nevertheless, as *Zhang* 1989 already pointed out, contact angle data delivers vital information for the understanding of the performance of fouled membranes, despite the hysteresis due to surface roughness and sample variation.

The used membranes in the initial stage of this study (PES and PSf) were quite similar in hydrophobicity. Therefore, it was hard to compare results with any degree of statistical significance. To counter this problem it was decided to add a membrane material to the study, which is fairly different in hydrophobicity in comparison to the named above. This material was cellulose, which is so hydrophilic that it causes water droplets to flatten out on the surface, making a determination of the contact angle impossible.

3.5 Extraction of organics from the membrane

Pulp liquors in the paper industry contain in addition to the main components, cellulose, hemicellulose and lignin also minor quantities of many other components. These components can only be dissolved in small amounts, since they are of pure hydrophobic or ampiphilic nature. They are more easily dissolved in organic solvents. Therefore these group of minor components are called **extractives.** The nonpolar extractives consist primarily of fatty acids, resin acids, waxes, alcohols, terpenes, sterols, steryl esters and glycerides. Lignans are the polar extractives. It is worth noting that these minor components are very likely to end up on the membrane, since they are of hydrophobic nature.

The extraction of these foulants from the membrane surface and pores is a good method to determine exactly what kind of organic substances are precipitating and even to quantify them. Extraction is not destructive and can reach even the foulants in the pores. Also, it will complement analytical data from the raw liquor showing what really ends up on the membrane. However, there is one big disadvantage: the type of extracted substance and the amount will depend largely upon the solvent used during the extraction process. A list of commonly used solvents can be found *in Levlin and Söderhjelm* 1998. Therefore, a wrongly chosen solvent could lead to a result, which does not include all the extractives precipitated on the membrane. To minimise the degree of the problem *Puro et al.* 2002 developed a modified extraction method, in order to get a good cross-section results of all the present extractives on the membrane. *Puro et al.* also investigated the extraction time necessary and the type of extraction in order to obtain best possible result.

3.5.1 Extraction procedure

The extraction was carried out with a Soxhlet apparatus. Detailed instructions about the method and equipment used can be found in *Puro et al.* 2002. The membrane was cut into small pieces and placed into an extraction tube and a solvent mixture of acetone/water (9:1) was added. Samples used were fouled PES and PSf membranes cleaned with NaOH over multiple operational cycles. The

vacuum freezing. The dried samples seemed to contain polymeric material from the membranes. Because this harms the gas chromatograph columns, the samples were diluted in 4 mL of RO water and extracted a second time with liquid-liquid extraction, in order to get rid of the polymeric material. After the liquid extraction the sample was again freeze dried. Before undergoing a gas chromatography analysis, the extractive components must be converted to volatile derivatives. In this study a silylation was carried out and then analysed in the GC. Gas chromatography is one technique used for separating and analyzing complex mixtures of materials. Materials used in the gas chromatograph (GC) must be volatile (they must vaporize quickly and easily at low temperatures).

The volatile liquid materials is injected into the column with a microliter syringe, heated at the injection port for quick vaporization, and then carried by the mobile phase (or carrier gas). The carrier gas is an inert gas that carries the sample from the injection port through the column, and into the detector. The rate at which the sample passes through the column depends on two parameters: 1) the size of the particle, and 2) how well it is adsorbed onto the column. Mixtures separate well only if there is a significant difference in at least one of these two parameters: affinity for the column material or size of the particle.

Once the molecules leave the column, they are subjected to a detector. A sample's identity can be determined by its retention time. Retention time is the time required for the maximum concentration of the solute to appear at the detector. This point forms a peak on the chart paper. One can compare retention times of unknowns with standards run under the same conditions to determine the identity of a sample. This is the "qualitative" application of the GC and the peak area can give the "quantitative" result. The final amount of the components were calculated with the following equation:

$$\frac{Extractives, mg}{area, m^2} = \frac{(sample\ peak\ area)(Standard\ amount, mg)}{(Standard\ peak\ area)(Membrane\ area)} \qquad (12)$$

The results will add to the results of the SSL analyses described in the next section.

3.6 Total organic carbon determination

The amount of total organic carbon (TOC) was used as a mean to analyze the degree of solid content in permeate and to calculate from that the retention of solids. Even though it takes not into account the permeation of salts it is regarded as sufficient, because the focus of separation is on the organic part and not on the salts.

The analysis was carried out with a TOC from SHIMADZU corporation /Japan, model No. TOC-5000 A. The measurement takes place as total carbon (TC) and is detected as CO_2 after a sample is injected into a combustion chamber. This analysis is not distinguishing between carbons being of organic or inorganic origin. When a liquid sample is introduced (100 µl) it is pumped into a combustion tube containing a catalyst. Here, sample components containing carbon are decomposed to CO_2 . The reactants from the combustion tube are then swept with a carrier gas (N or pure air) into a inorganic carbon reaction vessel, where possible remaining inorganic carbon is decomposed to CO_2. The escaping carrier gas containing now both inorganic and organic carbon as CO_2 is then dehumified and passed through an scrubber to remove possible harmful halogens (e.g. chlorine). Finally an infrared gas analyzer detects the amount of CO_2. The absorption peak area is proportional to the amount of carbon dioxide. This relationship between CO_2 concentration and peak areas must be determined prior by the operator with the help of standard solutions.

3.7 Mass analyses of SSL fractions

After fermentation spent sulphite liquor contains salts, ligneous material (e.g. lignosulphonates) and extractives. The values differ, due to different production methods, wood composition and different analytical methods. For this project it is thought useful to analyse the following components in spent sulphite liquor.

- Water content and dry weight
- Ash and Ca content
- Acidic groups of lignosulphonates

The following spent sulphite liquor samples have been characterised:

- Spent sulphite liquor: VHV-S and VS-850. Both are gained from a calcium bisulphite digesting process, and differ due to their different feed of wood, which leads to a different composition in lignosulphonate.

Interestingly, product VS-850 showed no product flux decline when filtered, the opposite of VHV-S. The reason for that is probably that VHV-S is made from softwood (Norwegian spruce) and VS-850 from a mixture of hardwoods. Hardwoods contain less extractives than softwoods and the ligneous material is different in chemical structure. Therefore, it was decided to carry out the study with VHV-S, the softwood product, in order to get a reasonably fouled membrane.

3.7.1 Water content and dry weight

The water and ash content was established with the official method from the Technical Association of the Pulp and Paper Industry (TAPPI).

- (T550 om-98) for water
- (T 413 om-93) for ash

The water determination is simply based on evaporating free water in a sample at temperatures above 100°C and weighing the sample before and after the evaporation process. The ashing process is based on the fact, that at 900°C all non-mineral material will combust and only salts will remain, like Calcium oxide. Again, the percentage of ash is determined by weighing the sample before and after ignition.

3.7.2 Calcium content

After the cooking and separation process, the lignosulphonates remain as anions, rather than acids, the metal ions become important as binders of lignosulphonate molecules. They are involved in the mechanism of building aggregates.

The Calcium content was determined by atomic absorption spectroscopy (AAS), following a further standard method, issued by Tappi, T 266 om-94.

The AAS is based on the observation, that atoms absorb only a certain amount of energy from a distinctive wavelength of light. To measure this absorption, a solution, which contains the dissociated salt, is dispersed into a flame. In the flame, the salt diverts into the atoms, where depending on the concentration of atoms, a certain amount of energy is absorbed from an external light source. The absorption of light follows the Lambert-Beer law, which is also used for normal UV-and light spectroscopy analysis.

3.7.3 Weak and strong acidic groups of LS

The strong sulfonic acid groups and the weak acid carboxylate groups in LS can be determined by an acid-base titration, *Katz et al.* 1984. However, the experimental procedure proposed was found not to be suitable for the sulphite liquor used in this project, probably due to variation of composition. Therefore, the method was modified.

The titration is based on the fact that weak acids, here Lignosulfonates, form a buffer solution if they are titrated with a strong base, here sodium hydroxide. Therefore, during the titration, the pH remains nearly constant.

Figure 3.15 shows a typical conductometric titration curve of spent sulphite liquor. Before titration, the acidic groups must be transformed into the hydrogen form by soaking with a sufficient amount of 0.1 M HCl. Then the pulp is dispersed in 450 mL of 0.001M sodium chloride prepared in deionised water. In this solution the hydrogen dissociates from the acid groups. The surplus of H^+-ions, which were right after the soaking not attached to the LS is then neutralised during the first step of the titration. This step is marked in the figure with No. 1, with the most rapid decreasing branch of the curve. If the surplus of ions is used up the slope decrease and leads into section No. 2. In this section the hydrogen ions are neutralised, which are dissociated from the sulphonic acid groups. Then near the first equivalence point, the hydrogen ions from the weaker carboxylic acid groups begin to dissociate and contribute to the measured conductivity, hence some curvature appears and leads into section No.3. Here, with further addition of sodium hydroxide, the weaker acid groups are progressively neutralised. In this region, there is little change in the conductance because of the low level of

hydrogen ions in equilibrium with the weak acid as it is being titrated. Beyond the second equivalence point, however, the conductance increases in proportion to the excess sodium hydroxide present. The two equivalence points are located by extrapolating and intersecting the three linear portions of the curve.

In order to see the three sections of the curve it is important to use a sufficient amount of HCl during the soaking process. If there is no surplus of hydrogen ions and only just the amount necessary to transform the acidic groups into the hydrogen group, no dissociation of the hydrogen will occur during the titration. If there is a surplus during the soaking an equilibrium of dissociated and non-dissociated hydrogen ions is established. Some already dissociated hydrogen ions must be present in the solution to start the neutralisation and the further dissociation of hydrogen ions from the acidic groups. The amount of base used for the total neutralisation of the hydrogen ions is exactly the amount, which is just necessary to transform the acidic groups into the hydrogen form.

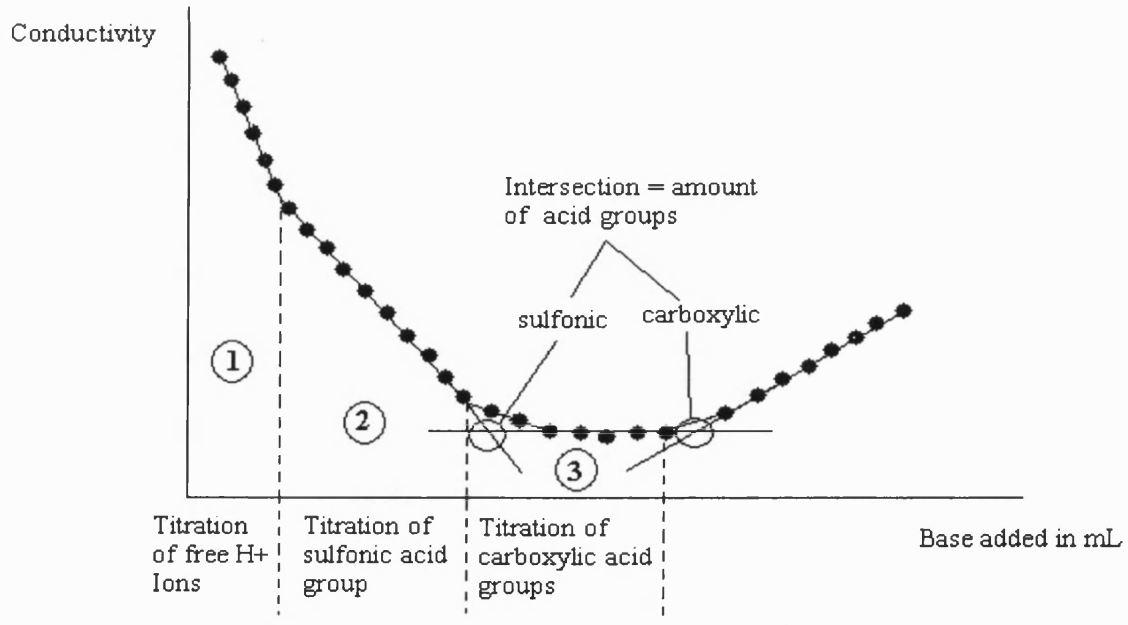


Figure 3.15: Conductometric titration curve of spent sulfite liquor

3.8 Summary

In this chapter the experimental set-up is described focussing on the reasons behind the rig design, which resulted in a straight forward and easy to handle set-up, but still delivering reliable results. The modules used were an in-house constructed plate and frame design for containing flat-sheet membranes. Self-made modules were used in order to control and manage fluid dynamics and flat sheet membranes were used in order to enable analytical investigations of the treated membranes. A detailed description and drawings of the rig and module are given, with how and why they were built as found in the present state. During the process of the study two different protocols were developed for the fouling and cleaning "cycles". The major difference is for protocol 1 an incomplete conditioning process and ambient temperature cleaning in comparison to protocol 2 with a complete conditioning and high temperature cleaning.

The rest of the chapter is focussed on analytical methods used for explaining filtration performance and interactions between membrane and fouling material and cleaning agents. It is explained why they are used for this study following the basic principles of these methods. Then the procedure of analysis is given with a brief literature review and practical experience gained during the study of the problems one is facing when applying these methods.

Zeta-potential determinations were used since surface charges have a significant influence on membrane separation properties and fouling tendencies. Beyond this, the zeta-potential is an excellent means to see the quality and quantity of change of potential caused by fouling and cleaning and can be used as a measure of the interaction between fouling substances and cleaning agents. The potential can be measured, when the counter-ions along a charged surface are moved due to pressure from one side of the membrane to the other side. The accumulating ions generate a potential that can be measured, which was done with a rig and module specially designed for this purpose at LUT. The most critical point for the use and interpretation of zeta-potential is that the EDL will overlap in very small pores and shrinking pores due to fouling, hence causing troublesome results.

Misinterpretation can possibly be avoided, when results are in line with other results, e.g. filtration data.

FTIR is a method to identify the structure of the membrane polymer or the fouling material. Beside this an assessment of the type of fouling and cleaning can be done with the degree of removal of foulants. The principle of FTIR is based on interaction of IR waves with certain bonds and functional groups of molecules. The absorbed IR frequency gives information about these bonds and functional groups and from this the whole molecule or polymer can be put together. The experiments were again carried out at LUT. The most critical point is that complex mixture of polymers or fouling material are hard to identify by the bands and peaks they are producing. Many different molecules contain similar bonds and functional groups, so that they will produce all the same peak, hence it is impossible to differentiate the molecules on the basis of their peaks.

The contact angle measurements give information about the wettability and therefore the hydrophobicity of the membrane. They will show the impact on fouling and cleaning upon the hydrophobicity. To measure the contact-angle a drop of water is placed on the membrane and depending on the surface energy, the water drop will bend with different angles on the side of the drop. The problem is that not only the surface energy influences the angle, also the surface roughness and the pore size and pore distribution will have an impact. Therefore the angles can show large variations, which makes it difficult to distinguish even small differences.

Extraction is an excellent method to investigate the quantity and quality of foulants. For this, the organic foulants are extracted with a solvent and finally analysed in a gas chromatograph. It should be borne in mind that the quantity and quality of foulants will depend to a varying degree on the solvent chosen for extraction. Finally, a mass analysis of the SSL is carried out.

Chapter 4

Results

and

Discussion

Part I

Analytical Data

4 Introduction

For investigating a complex problem such as fouling and cleaning, it is crucial not to draw conclusions based upon results from a single investigation method. Therefore, several tools were used to investigate the fouling layer material, such as FTIR and extraction. Zeta-potential and contact angle methods were used to determine changes at the membrane surface. Also, for the performance the main criterion is the evaluation of the product flux and the pure water flux, but retention needs to be presented as well to complete the picture. The Results and Discussion section is divided into two chapters; first the results and discussion of analytical data and second the results and discussion of the filtration data. Each chapter is subdivided into the results obtained for filtration following protocol 1 and protocol 2. In order to help the reader fully understand the experimental work carried out, a road map is drawn as can be seen in Figure 4.1(next page).

The aim of this experimental study was to examine membrane performance over short and long term, and investigate the synergetic relationship between process parameters.

In this chapter the results of the surface analysis are presented. They will complement the results from the filtration experiments and conclusions drawn from the surface analysis will help and support to explain the filtration results.

Five analytical tools were chosen for the work:

- Extraction: for qualification and quantification of fouling material
- Contact angle measurements as a measure of changes in the hydrophobicity of membrane surfaces at different numbers of cycles
- ATR-FTIR: for qualification and quantification of fouling material at different cycles
- Zeta-potential measurements as a means to establish the degree of interaction between fouling material, membrane material and cleaner.
- Atomic force microscopy: Pictures were taken of virgin, fouled and cleaned membranes, which give essential information about pore size distribution and

surface roughness. The pictures of the virgin membranes are displayed in the Material and Methods chapter. Further pictures and information can be found in *Chukwuemeka* 2002.

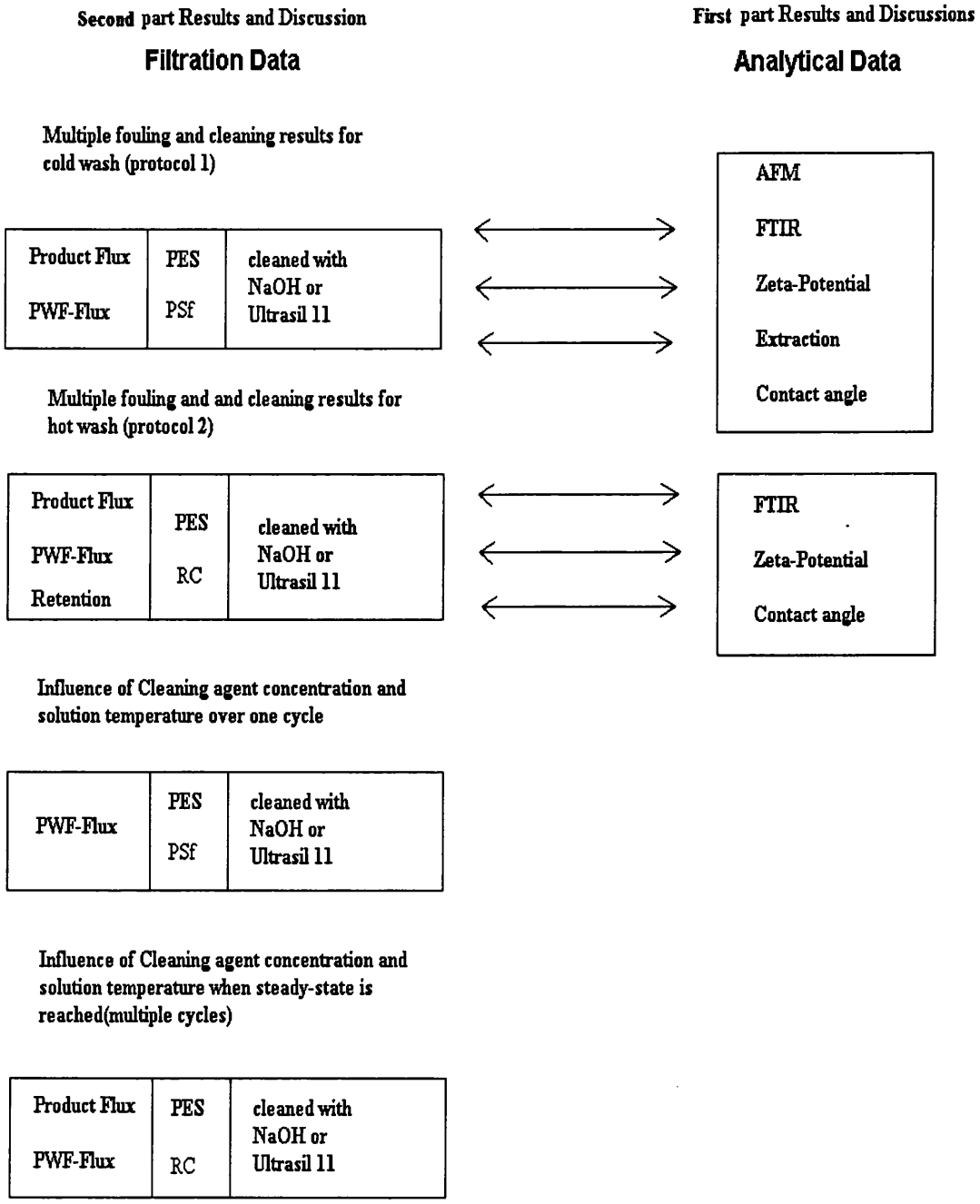


Figure 4.1: Overview of the separation and presentation of results

4.1 Contact angle

The measurement of contact angle is a method to estimate the surface wettability of a given material. Even though the measurements were carried out 20 times, the standard deviations were high, which makes small changes in wettability hard to detect. However, the results still make sense in context with the other results. As already mentioned, the regenerated cellulose is extremely hydrophilic and droplets disappear immediately when they touch the surface. Therefore, only results for PES and PSf are presented in Table 4.1.

The contact angle results in Table 4.1 for PES membrane reveal the impact of NaOH and *Ultrasil 11* cleaning on wettability. The higher hydrophilicity of an unconditioned membrane in comparison to a conditioned arises from the presence of glycerine, which effectively represents a kind of temporary coating of the membrane to prevent it from drying out. Glycerine with its three hydroxyl groups is highly water soluble. The problem with removing it completely arises from glycerine in narrow pores. These pores are hard to wet, especially when a conditioning is carried out for a short period and at ambient temperatures. Therefore, some glycerine remains in pores when conditioned according to protocol 1. *Chukwuemeka* used membranes conditioned according to protocol 1. It explains why his membranes still appear to be more hydrophilic than the virgin PES membranes conditioned according to protocol 2. It should be noted that the angle values obtained from *Chukwuemeka* are remarkably similar to the results obtained in this study, but with smaller standard deviations. There is one single exception, which is hard to explain. This exception is for 20 x fouling and 20 x NaOH cleaning may be a wildpoint.

As expected when the membrane is fouled the hydrophobicity increases. When cleaned with NaOH the contact angle changes slightly back to more hydrophilic values. But as already mentioned, the standard deviation when measuring the angles was bigger than the change, so a statement should be treated with caution.

Table 4.1: Contact angles of virgin PES membrane and fouled and cleaned PES membrane. Average and Standard deviation values obtained from 40 measurements. (Conditioned=1.5h with pure water at 50°C). For comparison reasons the values in brackets are obtained with the same membranes but different sheets by Chukwuemeka 2002.

	Average	StDev	Average	StDev
virgin (unconditioned)	52.4	2.4	52.4	2.4
virgin (conditioned)	64.4 (60.0)	2.9 (1.79)	64.4 (60.0)	2.9 (1.79)
1x fouled	70.3 (67.2)	3.5 (0.59)	70.3 (67.2)	3.5 (0.59)
Cleaned with	NaOH	NaOH	Ultrasil 11	Ultrasil 11
1x fouled-1x cleaned	68.9 (71.6)	4.1 (0.86)	56.9 (69.0)	3.1 (0.56)
2x fouled-1x cleaned	77.3	2.5	59	3.2
2x fouled-2x cleaned	67.5	2.8	61.6	3.8
20x fouled-20x cleaned	93.6 (71.5)	1.9 (2.20)	/	/
14x fouled-14x cleaned	/	/	71.9 (67.8)	5.5 (1.03)

In general when cleaned with sodium hydroxide the surface becomes more and more hydrophobic probably reaching a plateau value. When cleaned with *Ultrasil 11*, the wettability changes back to a value close to the value found for the virgin membrane. Obviously, the surfactants, in particular the non-ionic ones, increase the hydrophilicity by adsorbing to the surface when cleaned. Remarkably, when a cold wash is carried out, almost no change in contact angle can be detected. The ambient cleaning temperatures lower the adsorptivity of the surfactants and an insignificant attachment takes place, which has no impact on the pure water flux results, see for example in Chapter 5, Figure 5.3 (a).

Table 4.2 Contact angles of virgin PSf membrane and fouled and cleaned PSf membrane. Average and Standard deviation values obtained from 40 measurenments. (Conditioned=1.5 h with pure water at 50°C). For comparison the values in brackets are obtained with the same membranes by Chukwuemeka 2002.

	Average	StDev	Average	StDev
virgin (unconditioned)	54.8	4.06	54.8	4.06
virgin (conditioned)	44.7 (52.9)	3.20 (1.32)	44.7 (52.9)	3.20 (1.32)
1 x fouled	(66.5)	(0.96)	(66.5)	(0.96)
Cleaned with	NaOH	NaOH	Ultrasil 11	Ultrasil 11
1x fouled-1x cleaned	(68.3)	(4.71)	(64.6)	(0.65)
20x fouled-20x cleaned	(82.7)	(5.24)	/	/
14x fouled-14x cleaned	/	/	(67.8)	(0.8)

Nevertheless from the first cleaning cycle onwards, repeated fouling also leads to a decreasing wettability. But even after many cycles the value never reaches the low value recorded when cleaned with NaOH.

In Table 4.2 the results for PSf membrane can be seen. Interestingly, the membrane becomes even more hydrophilic when glycerine is completely removed. Once again, if the removal is incomplete (using protocol 1→ results *Chukwuemeka)*, the trend towards more hydrophilic values is less pronounced. Also here as expected, when fouled, the surface becomes more hydrophobic. When cleaned with sodium hydroxide, the wettability does not really recover and becomes increasingly hydrophobic with repeated cycles. When cleaned with *Ultrasil 11* at ambient temperatures the surface becomes more hydrophilic again due to the adsorption of surfactants. Even so, the recovery of wettability is much less pronounced as was found after cleaning with *Ultrasil 11* at high temperatures.

4.2 Extraction

The extraction of foulants was carried out for PES and PSf membrane. The results can be found in Figure 4.2.

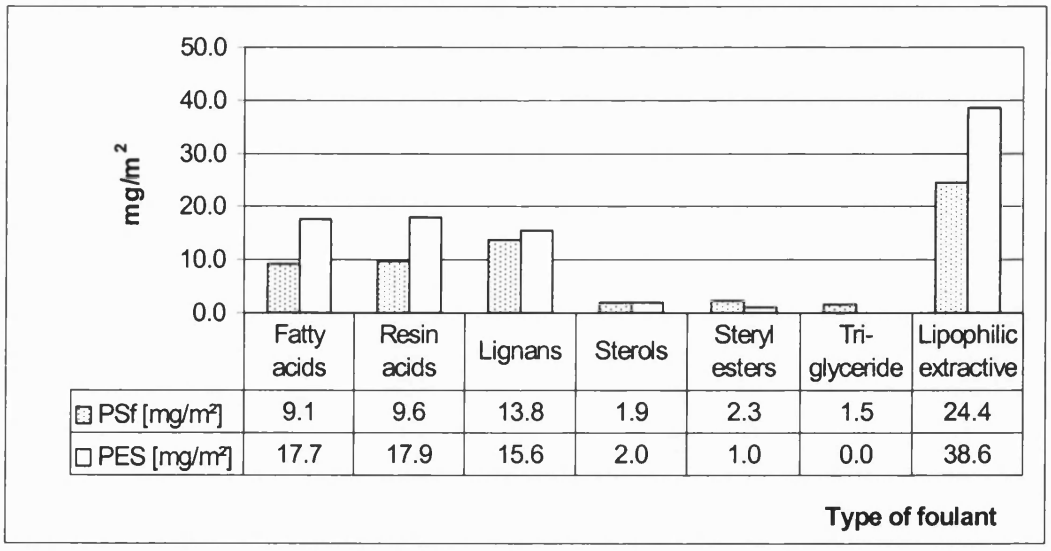


Figure 4.2: Extracted foulants on 20 times fouled and cleaned PES and PSf membrane. Protocol 1; 0.5wt% NaOH, 22°C, 1.9 ms^{-1}. Hydrophilic Lignans are not included in Lipophilic extractives.

On the right side of the graph the amount of lipophilic extractive is displayed for PES and PSf membrane. Lipophilic extractives represent the sum of all the different types of extractives found, except the hydrophilic Lignans. With the comparison of the amount of lipophilic extractives adsorbed on the PES and PSf membrane one can get a good idea of the hydrophobicity of the membrane material. Given the fact that on PES membrane almost 1/3 more lipophilic foulants have adsorbed than on PSf, it can be concluded that the PES material is more hydrophobic than PSf. This is confirmed also by the contact angle measurements as well. On the other hand, the PES membrane clearly has a higher surface area. Therefore, the higher amount of foulants found on PES could be due to this higher surface area, rather than due to the higher hydrophobicity. According to the contact angle results the differences between PES and PSf are rather small, hence the impact of the higher surface area for PES seems to be significant. In addition the more hydrophilic Lignans adsorb to a very similar degree on both membranes.

The main foulants for both membranes are fatty acids, resin acids and lignans, and most likely lignosulphonates. In wood pulp in general, about 25% of the total amount of lipophilic extractives at pH 5 are fatty and resin acids. About 5 % of them are dissolved in the pulp, and only this dissolved fraction was found to be on the membrane. Resin acids and lignans are difficult to differentiate. Both groups have as core elements a net of aromatic groups and aliphatic side chains with a different number of functional groups, such as hydroxy, ether, ester and sulphones. Most resin acids are isomers or structurally close relatives of abietic acid. The formulas of the eleven most common resin acids extracted from wood can be found in *Luong* 1999. Lignin is a much more complex molecule and is built up of three monomer units. They are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The approximate structures can be found in *Roberts* 1993.

4.3 ATR-FTIR Results

Infrared spectroscopy is a good method to identify and quantify even small changes in the degree of fouling. The identification of chemical structures is possible, but needs plenty of training and the danger of false interpretation remains. The problem is that the obtained spectra are compared with reference spectra from libraries. Single peaks of the spectra are compared with peaks of known peaks of functional groups. But these reference spectra and peaks are obtained from pure material. In reality materials are very often a blend of different substances. This is particularly true for polymers, which contain ingredients in order to tailor the polymer for a certain task. These ingredients will alter the spectra, and then it becomes almost impossible to relate the peaks of the functional groups to the different polymers used for the making of the membrane. However, if this is borne in mind, the FTIR is still a good tool to retrieve information. Therefore, an attempt has been made to interpret the material of the virgin membranes used. Subsequently it will be shown how glycerine affects the spectra. Finally, the influence of fouling and cleaning upon FTIR spectra is considered.

4.3.1 Virgin membranes

The virgin membranes investigated were made of PES, PSf and RC (Figure 4.4 a-c). For PES, PSf and RC membranes reference spectra were found in *the Perkin-Elmer* search library and reference book, *Hansen* 1987. The best fit for PES was a substance called Polyphenylene ether sulphone (see Figure 4.4(a)), which has ether phenylsulphone linkage as it can be found for polyethersulphone (see chemical structure in Figure 4.3). For regenerated cellulose membrane the best substance found was cellulose acetate, but also pure cellulose, see Figure 4.4(b). The regenerated cellulose is produced from cellulose acetate by *Hoechst* company. The conversion process back into cellulose appears to be incomplete, so that in the virgin regenerate cellulose membrane can still be seen peaks from cellulose acetate (e.g at 1750, 1250 and 600 cm^{-1}). In the spectra for phenyleneethersulphone there is only one peak missing in comparison to the PES spectra, which is at 1667 cm^{-1} (band width 1700-1640 cm^{-1}) The PES membrane

was supplied by *Mycrodyn- Nadir GmbH*, Wuppertal Germany. The active layer is supposed to be a blend of polyethersulfone with polyvinylpyrrolidone as copolymer on a polypropylene carrier, *Ernst* 2000. So, the peak at 1667 cm^{-1} could result from that copolymer, which has the function of increasing the hydrophilicity of the polymer mixture. Indeed, the best match to such a peak according to *Socrates* 1994 is vinyl ester CH_2=CHOCOR. Unfortunately the reference spectrum for PES stops at about 600 cm^{-1} but the spectra for PES was obtained from 4000-500 cm^{-1}, so ca. 100 cm^{-1} are missing. Since the reference spectrum for PES has a tendency to increase at 600 cm^{-1} it is assumed that it will follow the spectrum of PES. The same problem occurs for the RC membrane and its reference spectrum.

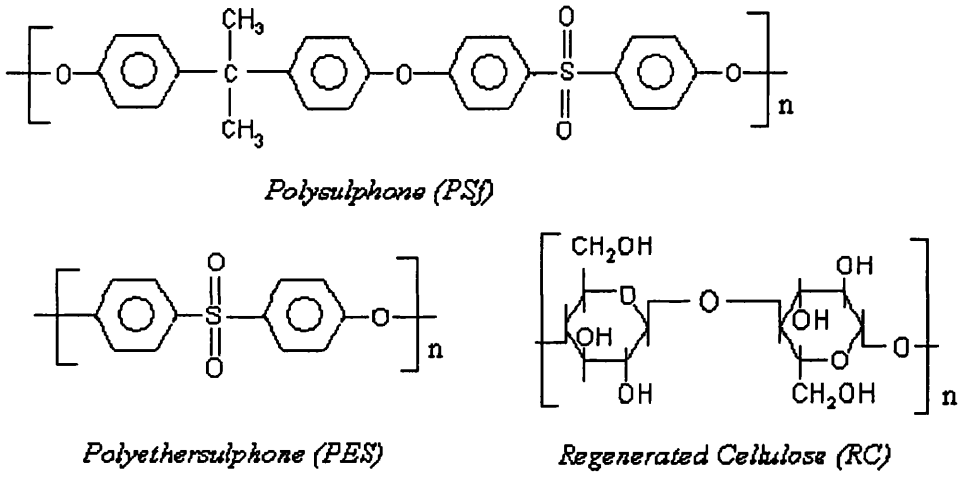


Figure 4.3: Chemical structures of membrane polymers

PSf is very similar to PES and a good comparison of these two virgin membranes can be found in Figure 4.4(a). The *Osmonics* polysulphone membrane displays a peak at 1065 cm^{-1} that is missing for the *Nadir* membrane. The search program indicates that this peak represents alkyl groups, such as methyl in polysulphone The peak at 550 cm^{-1} in PES stands for aromatic sulphone. The same peak for aromatic sulphone can be found at 720 cm^{-1} in PSf. The difference in wavenumber is probably due to different linkage with the rest of the polymer. The different intensities of the peaks result from the different surface roughness and pore size distribution of the two membranes.

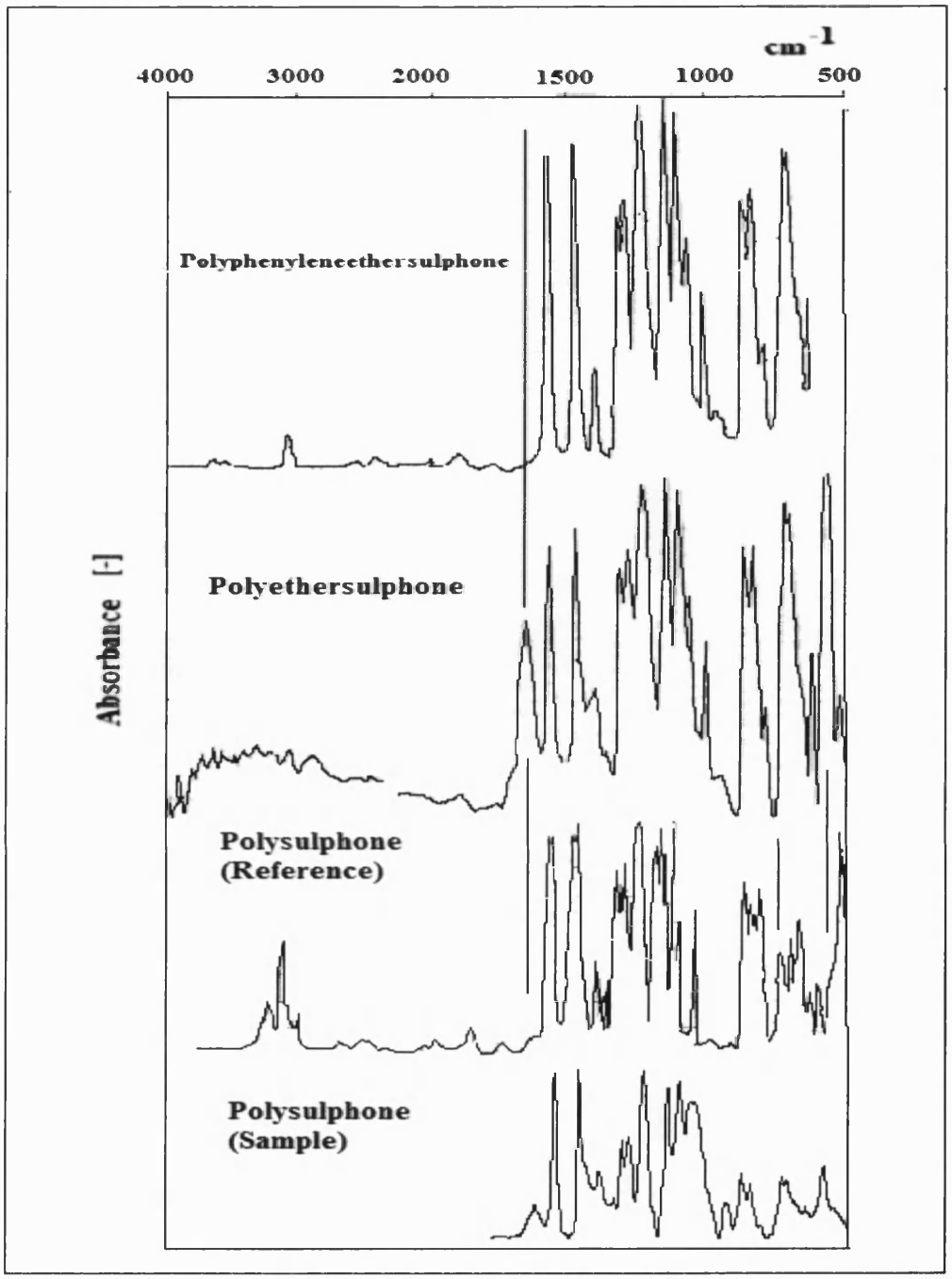


Figure 4.4(a): Top spectra; Polyphenyleneether sulphone (from Perkin-Elmer search library),second spectra from top; PES-virgin membrane, third spectra from top; Polysulphone spectra (from Aldrich search library), bottom spectra; Polysulphone sample.

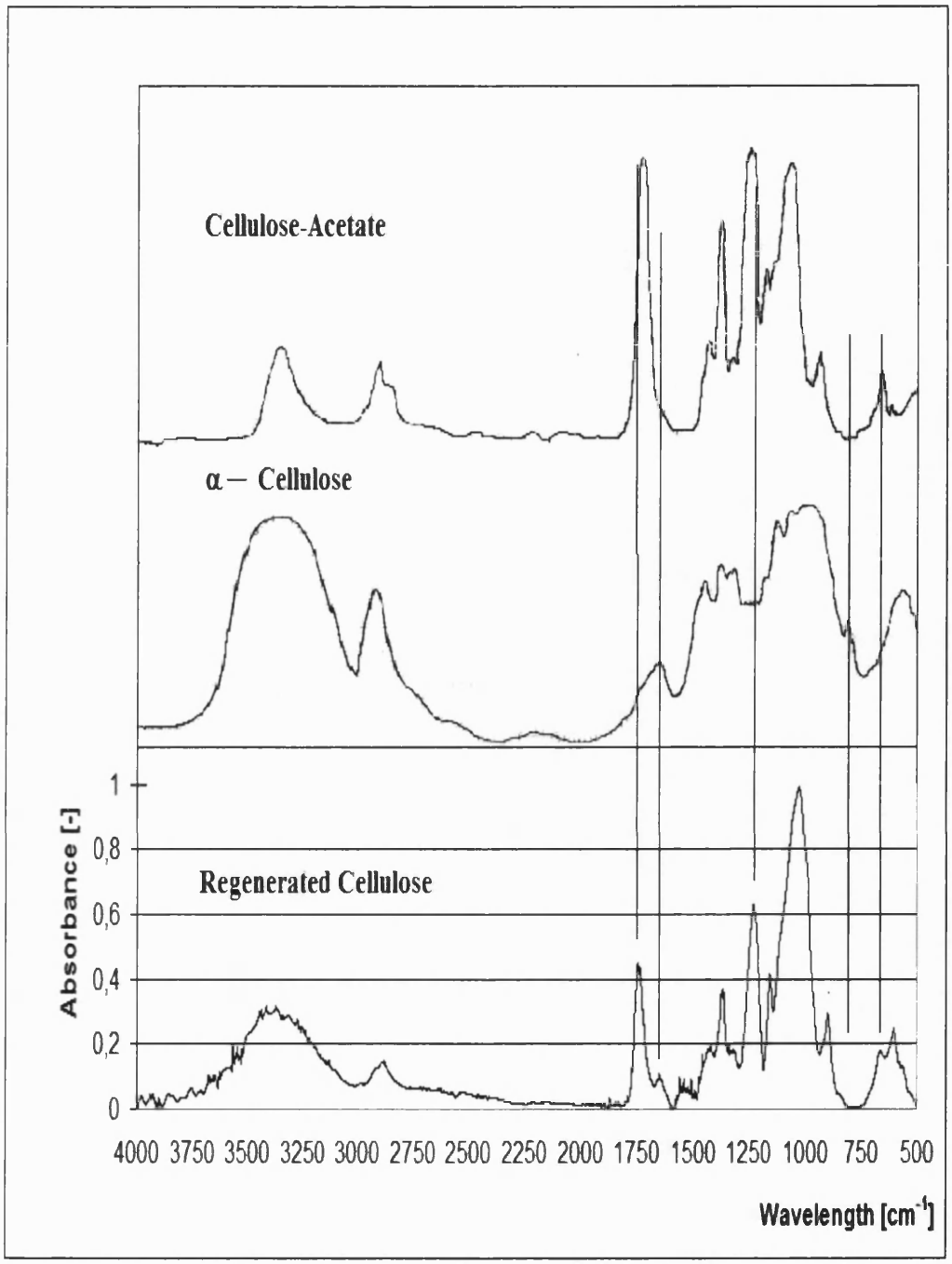


Figure 4.4(b): Bottom spectra; RC-virgin membrane (regenerated cellulose); middle spectra; cellulose, top spectra; Cellulose acetate. Middle and top spectra from Hansen 1987.

The Perkin-Elmer search program found follows the functional groups displayed in Table 4.3. The problem with these possible structural units (PSU) found is that many can be part of various chemical structures. For instance, "aromatic compound" is quite general and can be found in the membrane polymer (PES and PSf) as well as in most foulants, like lignosulphonates and resin acids. None of the PSU is actually uniquely related to a certain substance. Nevertheless, all peaks were compared to reference spectra (*Hummel* 1978, 1984 and *Socrates* 1994) and an attempt was made to identify foulants, particularly the lignosulphonates. An interpretation of peaks can be found in *Weis et al.* 2003.

Table 4.3: Possible structures found by the Perkin-Elmer search program for virgin and fouled and cleaned PES and PSf membranes

Class Number	*PSU*	Possible Peaks (cm^{-1})
201	Alkyl group (general)	*3330,2860,1490,1235, 1150, 1100, 1070*
259	Aromatic compound	*1580, 1490, 1320, 1290, 1240, 720, 700*
267	Aromatic compound, 1,4 – substituted	*1495, 830*
4906	Carbonyl	*1650*
402	Hydroxy – Group	*3330, 1235, 1150, 1100, 1000, 1070, 875*
511	Aliphatic alcohol	*3330, 2940, 1490, 1010*
2710	Aryl – Ether	*1580, 1490, 1295, 1150, 1100*
2724	Phenoxy – General	*1580, 1490, 1295, 1235, 1150, 1100, 1070, 870,830,720,700*
2906	Aromatic primary amine	*1580, 1490, 1295*
4002	*Aromatic sulphone*	*1580, 1490, 1320, 1290, 1150, 1100, 1070, 870,830,720,700*

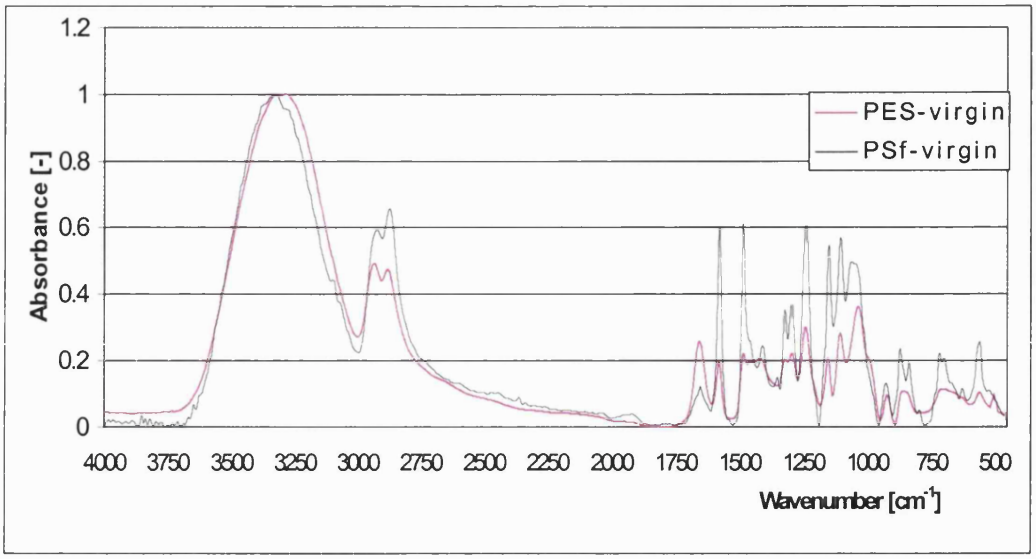


Figure 4.5: Spectra of virgin PSf and PES membrane after cold conditioning for 15 min. (protocol 1). The two large peaks between 3600 and 2600 comes from glycerin, which was not completely removed.

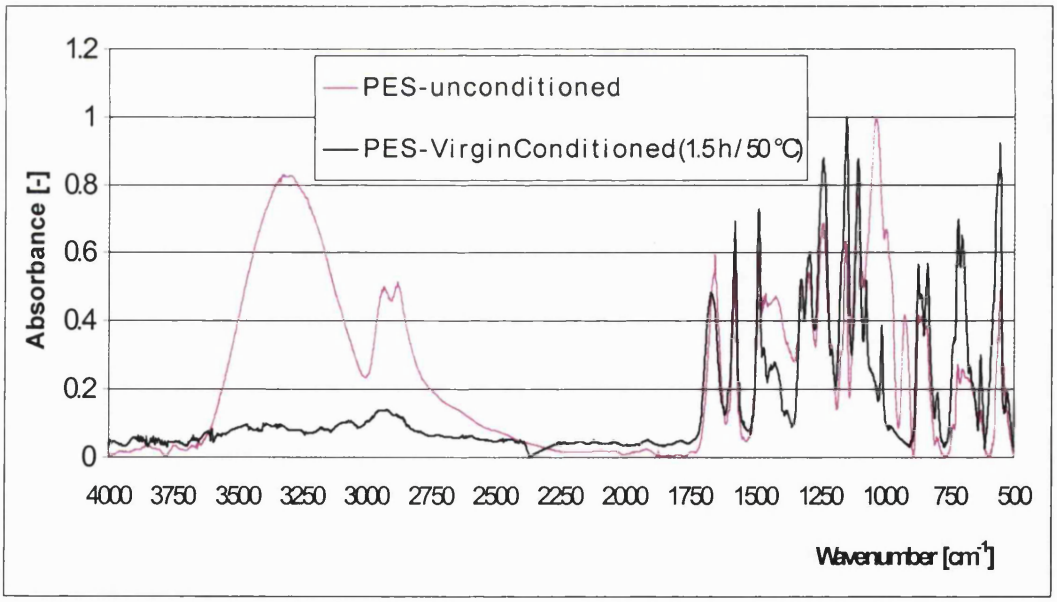


Figure 4.6: Comparison of virgin PES membrane in unconditioned and fully conditioned state.

4.3.2 Glycerine removal

As already seen for the contact angles, the glycerine affects the wettability. Glycerine results in a large peak at 3300 cm^{-1} as seen in Figure 4.5 and Figure 4.6 above. When these two figures are compared it becomes clear that cold conditioning for 15 min at 1 bar pressure is not sufficient, and the spectrum still looks like the unconditioned virgin membrane, where the big glycerine peak can still be fully seen. Because protocol 1 was used in the initial stages of this study, glycerine was not removed sufficiently from the membrane and caused then problems with the resolution of FTIR spectra. But the resolution is very important when trying to determine small changes due to fouling and cleaning. Therefore, FTIR results from the membranes treated according to protocol 1 delivers only limited information. Nevertheless, they will be displayed for completeness and a brief discussion will be given.

4.3.3 FTIR spectra for "cold" cleaning

In the following two Figures 4.7 and 4.8 the spectra for PES and PSf virgin and fouled and cleaned membrane are displayed. The spectra result from the initial stage of the study. As a conclusion of these results it was decided to introduce a

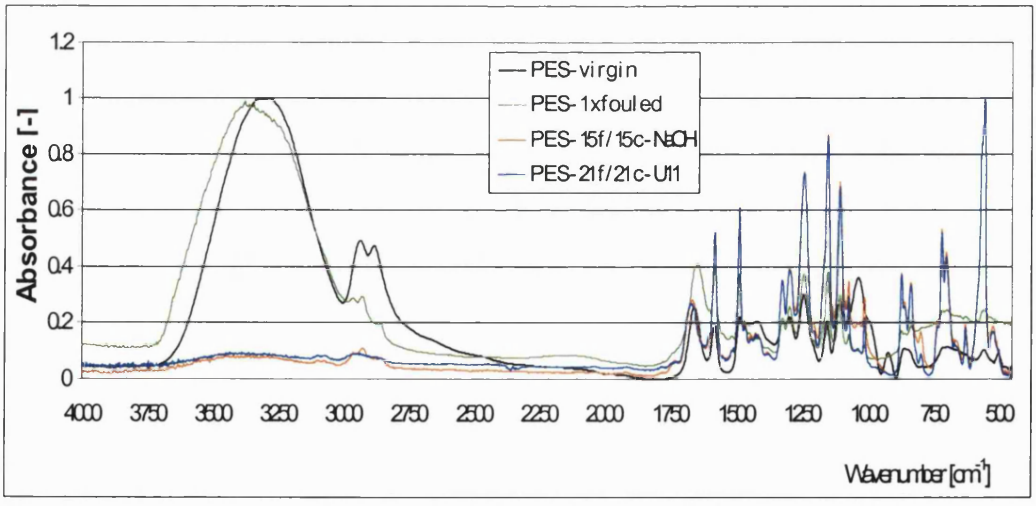


Figure 4.7: Spectra of virgin PES and VHV-S fouled and NaOH/Ultrasil 11 cleaned PES membrane after cold conditioning for 15 min, (protocol 1; 0.5wt%, 22°C, 1.9 ms^{-1}).

membrane material in the study which is more hydrophilic than PSf and where the IR spectra would exhibit different peaks to the polysulphone peaks seen in the spectra for PSf and PES. It was assumed that differences could be then more easily spotted due to the bigger difference in hydrophilicity and material composition.

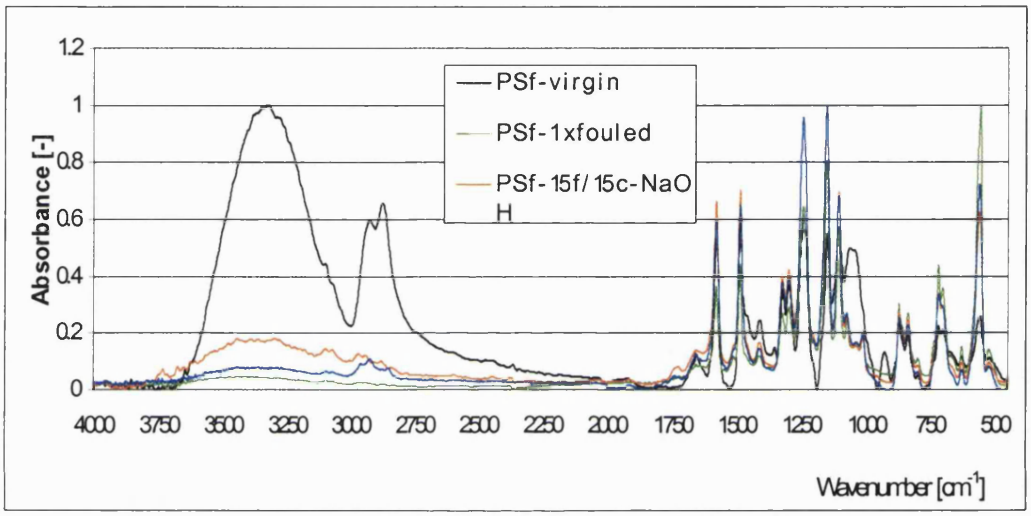


Figure 4.8: Spectra of virgin PSf and VHV-S fouled and NaOH/Ultrasil 11 cleaned PSf membrane after cold conditioning for 15 min.(protocol 1; 0.5wt%, 22°C, 1.9 ms^{-1}).

The most eye-catching occurrence is the disappearance of the glycerine peaks when the number of cycles is progressing. A detailed listing and explanation of peaks appearing and respectively disappearing due to fouling and cleaning can be found in *Weis et al.* 2003 and will not be repeated here. The publication can be found as an attachment to this thesis. In general the bands between 1700 and 500 cm^{-1} reveal only that *Ultrasil 11* appears to clean better than NaOH over long term, since the spectrum of the *Ultrasil 11* cleaned membrane is closer to the spectrum of virgin membrane than the one for NaOH.

4.3.4 The FTIR spectra of "hot" cleaning

In the following pages the FTIR spectra of single and multiple fouled and cleaned PES and RC membranes will be shown when cleaned with NaOH or *Ultrasil 11* according to protocol 2. For each membrane and cleaning solution two spectra are displayed. One for the wavenumbers between 4000 and 500 cm^{-1} and from this the section from 1800 to 500 cm^{-1}, in order to determine better the differences between the peaks at different stages. The peaks do not give only information about the chemical structure, they also reveal the fouling and cleaning mechanisms. Therefore, a statistical analysis was carried out with certain peaks to see what impact cleaning has on different membranes. The height of the peak will be directly related to the degree of fouling/removal and therefore a change of peak height will give information about the cleaning mechanism.

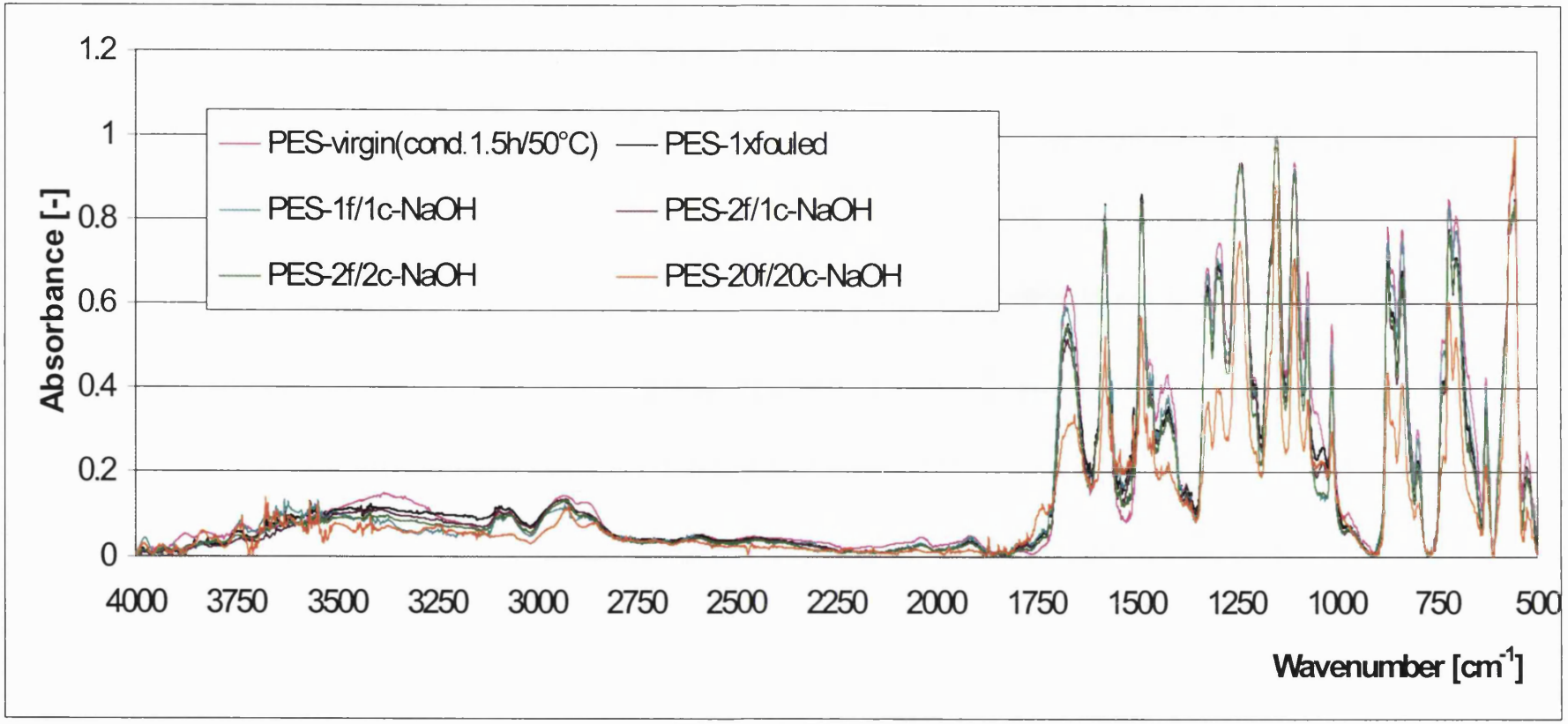


Figure 4.9: Spectra of virgin PES and multiple VHV-S fouled and NaOH cleaned PES membrane .(protocol 2; 0.5wt%, 60°C, 1.9 ms^{-1}).

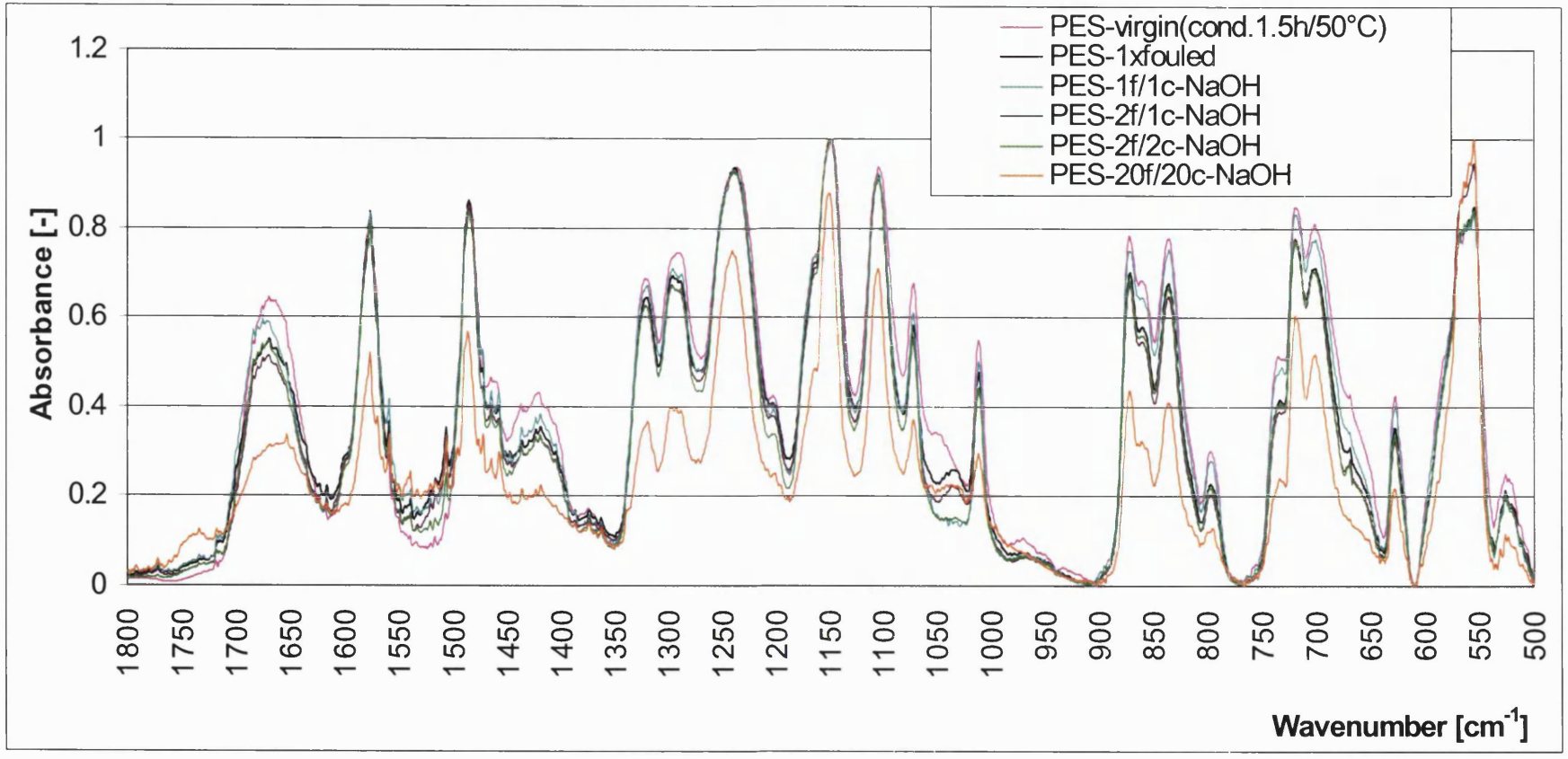


Figure 4.10: Spectra of virgin PES and multiple VHV-S fouled and NaOH cleaned PES membrane .(protocol 2; 0.5wt%, 60°C, 1.9 ms^{-1}). The wavenumber range between 500 and 1800 cm-1 was selected for better visibility.

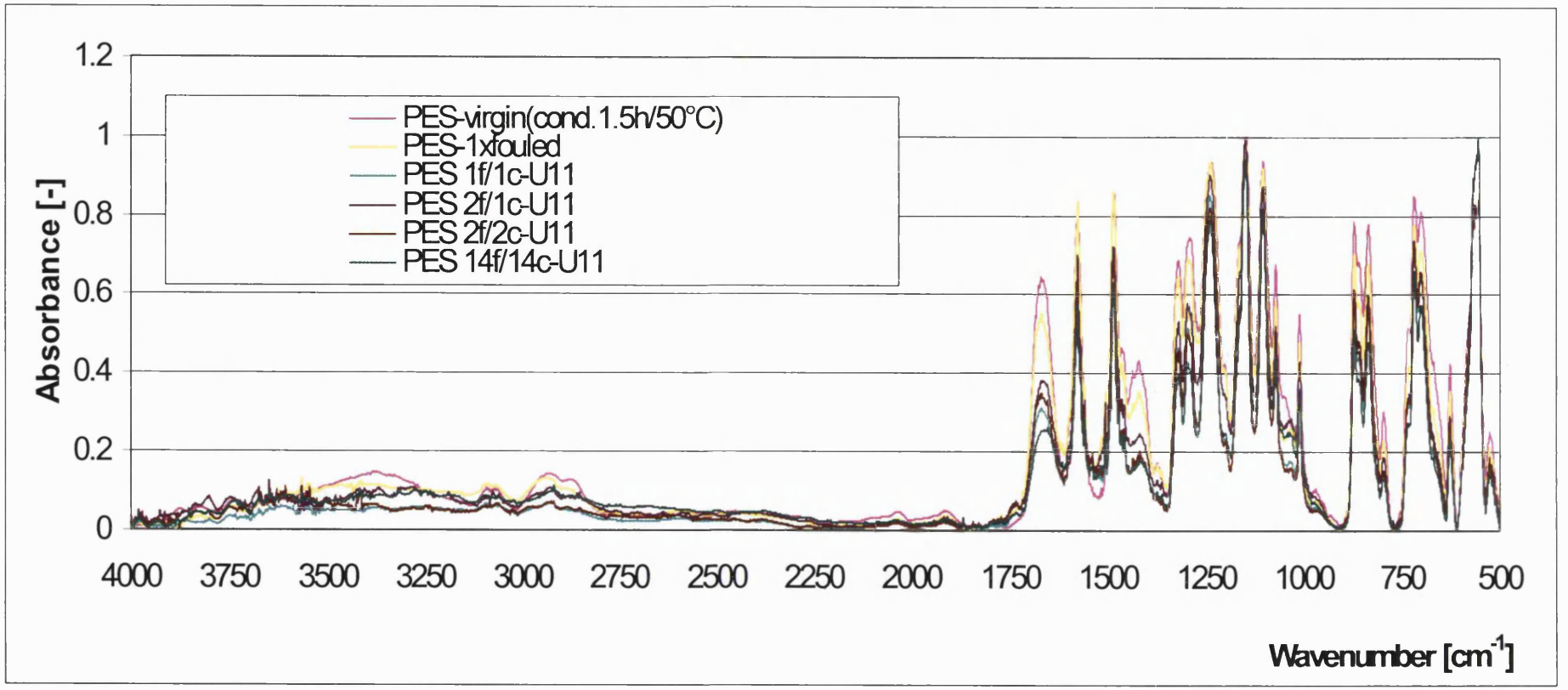


Figure 4.11: Spectra of virgin PES and multiple VHV-S fouled and Ultrasil 11 cleaned PES membrane .(protocol 2; 0.5wt%, 60°C, 1.9 ms⁻¹).

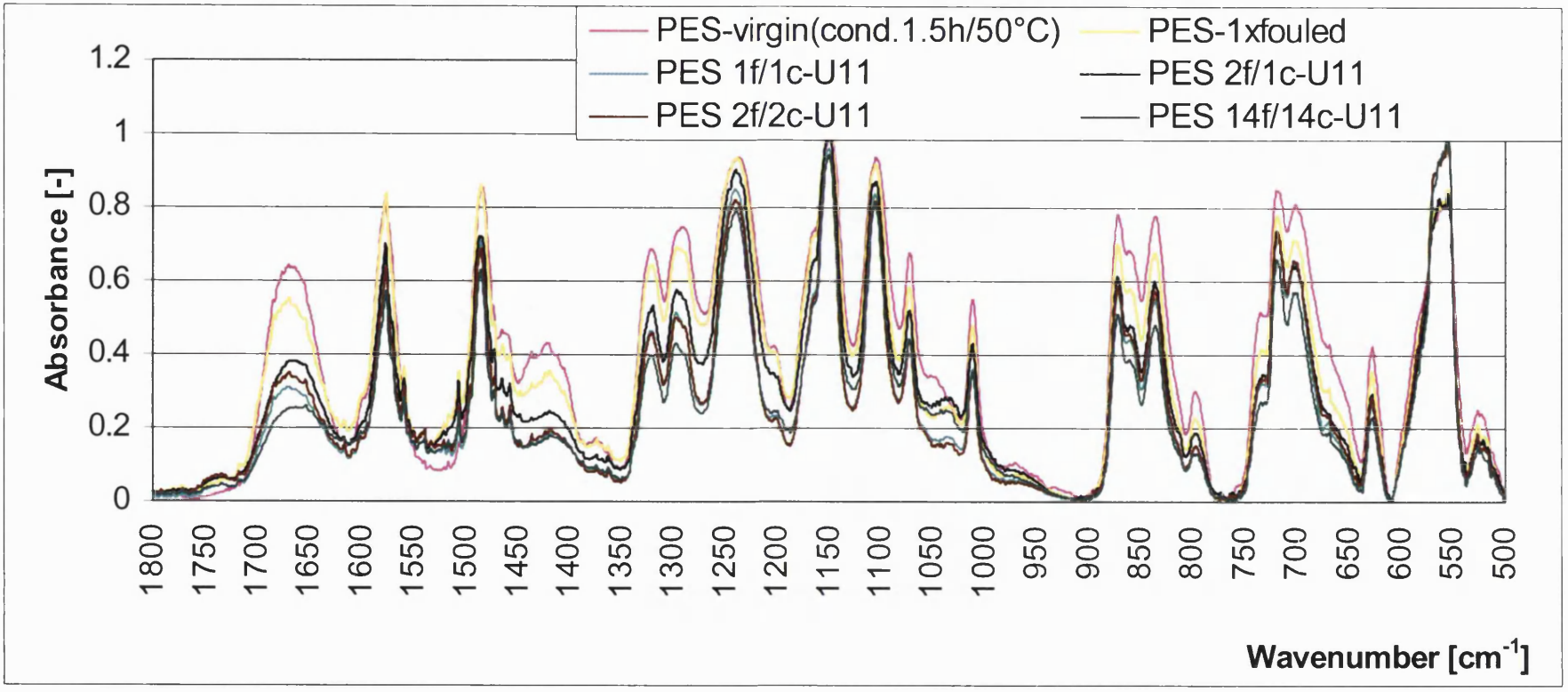


Figure 4.12: Spectra of virgin PES and multiple VHV-S fouled and Ultrasil 11 cleaned PES membrane (protocol 2; 0.5wt%, 60°C, 1.9 ms^{-1}). The wavenumber range between 500 and 1800 cm-1 was selected for better visibility.

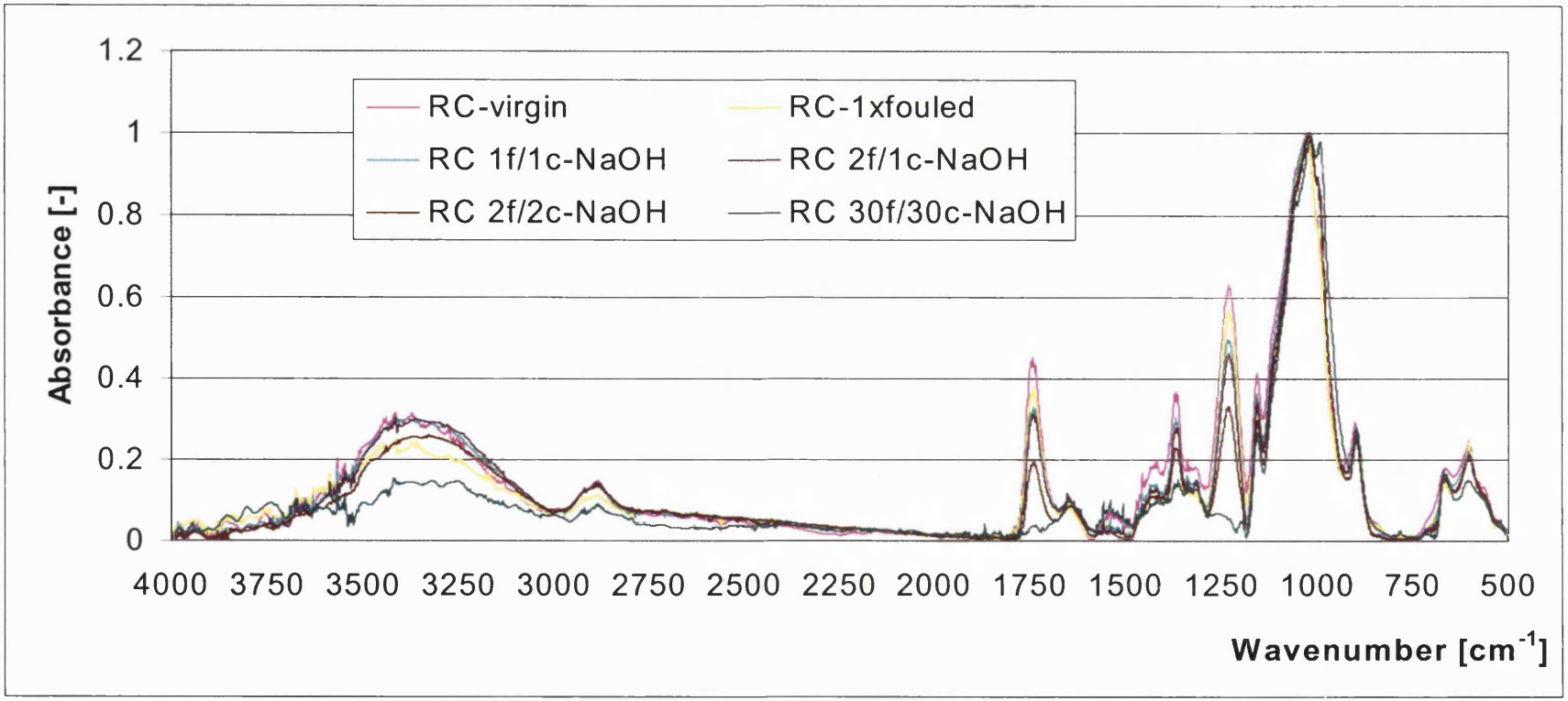


Figure 4.13: Spectra of virgin RC and multiple VHV-S fouled and NaOH cleaned RC membrane .(protocol 2; 0.05wt%, 0°C, 1.9 ms^{-1}).

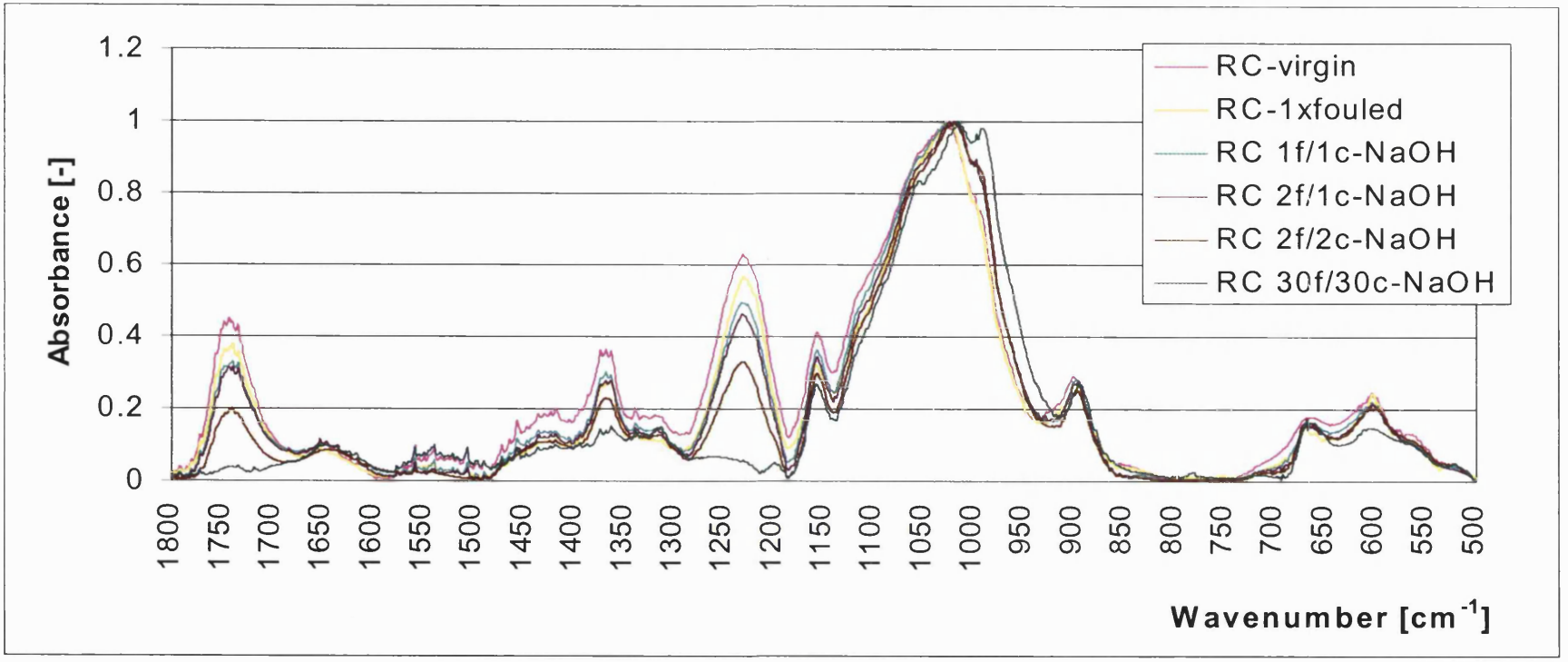


Figure 4.14: Spectra of virgin RC and multiple VHV-S fouled and NaOH cleaned RC membrane. (protocol 2; 0.05wt%, 40°C, 1.9 ms^{-1}). The wavenumber range between 500 and 1800 cm-1 was selected for better visibility.

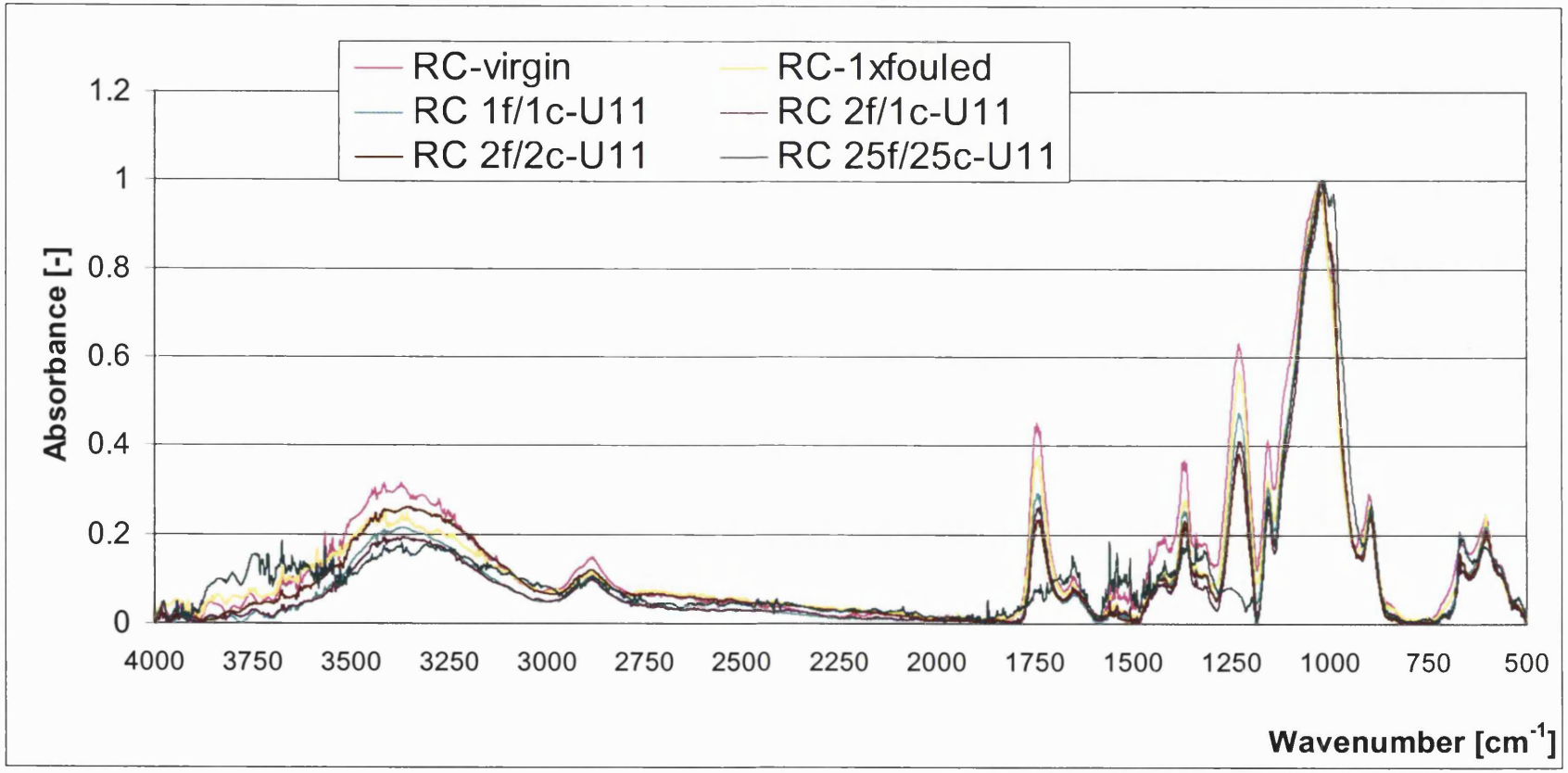


Figure 4.15: Spectra of virgin RC and multiple VHV-S fouled and Ultrasil 11 cleaned RC membrane .(protocol 2; 0.05wt%, 40°C, 1.9 ms^{-1}).

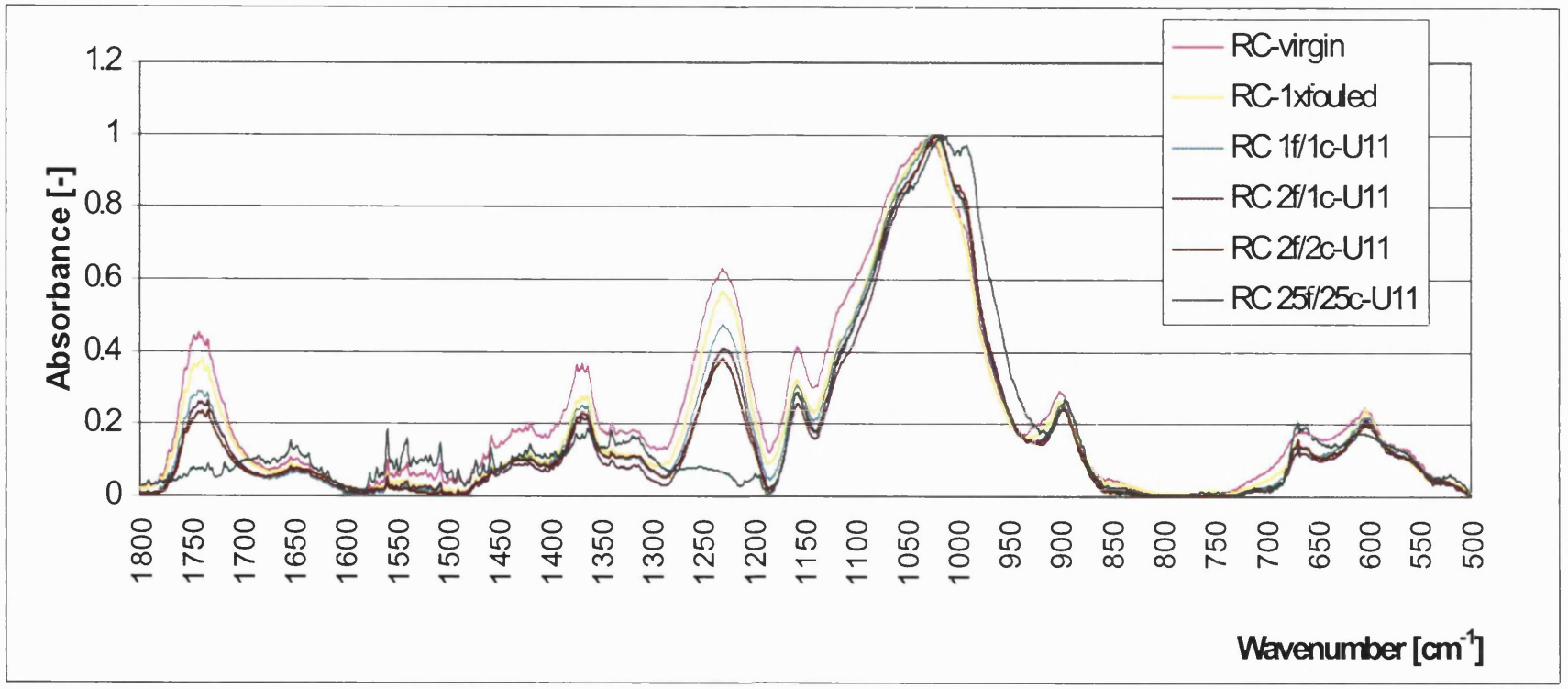


Figure 4.16: Spectra of virgin RC and multiple VHV-S fouled and Ultrasil 11 cleaned RC membrane. (protocol 2; 0.05wt%, 40°C, 1.9 ms^{-1}). The wavenumber range between 500 and 1800 cm-1 was selected for better visibility.

4.3.5 Analysis of selected peaks

FTIR can be used for quantitative analysis. This is rather straightforward for single components and is also possible for multicomponent analysis, but is nevertheless laborious. The only thing one needs to know in advance is the nature of the components in order to obtain standards and a mathematical model. This was not possible in this study, since the exact structure of the membrane, the fouling material and the surfactants in *Ultrasil 11* are not known. Particularly the fouling material is the source of the biggest problem. Even though the fouling material can be divided into major groups, these groups still contain hundreds of complex subgroups of molecules, all with different absorptivity values. The absorptivity is a fundamental physical property of the molecule and needs to be known before carrying out standards. That means in this study the absolute amount of foulants or surfactants adsorbing on the membrane surface cannot be determined. However, what can be detected is the degree of change of bands. This change will still give vital information about the degree of removal, cleaning mechanism and interaction between membrane, foulant and cleaner. To do so, only the change of peak height or peak area needs to be noted for different stages of fouling and cleaning. The peak height or area is directly proportional to material concentration.

For the sample preparation it was decided to prepare samples for the fouling and cleaning step until the second cycle (2x fouled and 2x cleaned) for each membrane and cleaning solution. When added to the samples resulting from the long term experiments it should give complementary information about what happens during the most crucial starting time of the process in relation to the state of the membrane after many cycles. The preparation of the samples is time consuming. Furthermore, cycles beyond 2 will not reveal much additional information which cannot be obtained from the first two cycles. Trends can be extrapolated from the results of these two cycles, especially since additional results exist from the state of the membrane after long term exposure to fouling and cleaning and should fit to the trend extrapolated from the results of the starting cycles.

Some bands within a spectrum do not change their peak height or area to any significant extent, whilst others show significant changes. This is typical for IR bands and results from the sensitivity of functional groups to the change of radiation due to build up of a fouling layer. Bands which show significant changes in height appear only in the low wavenumber region (>1800cm^{-1}). The depth of penetration is dependent on wavenumber. The penetration depth goes down as the wavenumber goes up. Thus low wavenumber light penetrates further into the sample than high wavenumber light. Therefore, the peaks in the spectra presented below 1800 cm^{-1} are from the membrane material functional groups. If a layer of fouling covers up these functional groups, these bands in the lower region will be more sensitive than peaks in the higher region and show therefore more changes due to fouling. So what can be seen is not the appearance of entirely new peaks resulting from the fouling material. The fouling layer is rather blocking out light and some functional groups of the membrane polymer reacting by increasing or decreasing peak height/area, because they are more sensitive than others.

When obtaining FTIR spectra one needs to work very carefully in order not to introduce errors resulting from the method employed. Sources of errors are the position and condition of the crystal. Both can be neutralised by obtaining the blank spectra. Membrane samples are sandwiched between the crystal and crystal holder. The process of sandwiching needs to be reproducible. Small changes in the pressure by which the membrane is pressed against the crystal will affect the penetration depth of light. But if small changes need to be detected it can alter the outcome. In the FTIR used in this study there was no method by which this pressure could be accurately adjusted. Another source of error was the natural distribution of foulants over the surface. To combat these error sources, three samples were cut from each membrane and the spectra obtained, then the peak heights of the selected most significant peaks were averaged and the standard deviation calculated.

The results obtained can be found in the appendix in Tables 8.1 to 8.4. A few peaks are wildpoints. These were abandoned in order to maintain the standard deviation below 5%. The average values are displayed for each membrane and cleaning solution in Tables 4.4(a-b) to 4.5(a-b). The results displayed in these

tables are then used to draw graphs to show clearly what is happening on different membrane materials when cleaned with different cleaning solutions (Figure 4.17 and 4.18).

Table 4.4(a): Averaged peak-heights of PES fouled and NaOH cleaned membranes.

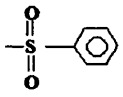
Membrane-Fouling and Cleaning State	Wavenumber				
	1667 cm^{-1} "Carbonyl" 	1280 cm^{-1} "Aromatic sulphone" 	850 cm^{-1} Aromatic sulphone	780 cm^{-1} Aromatic sulphone	720 cm^{-1} Aromatic sulphone
PES-Virgin	0.68	0.74	0.66	0.3	0.53
PES-1 x fouled	0.55	0.68	0.57	0.23	0.42
PES- 1f/1c-NaOH	0.56	0.7	0.65	0.28	0.48
PES- 2f/1c-NaOH	0.52	0.68	0.55	0.22	0.39
PES- 2f/2c-NaOH	0.54	0.67	0.55	0.22	0.4
PES- 20f/20c-NaOH	0.26	0.37	0.29	0.11	0.22

Table 4.4(b): Averaged peak-heights of PES fouled and Ultrasil 11 cleaned membranes

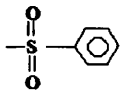
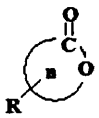
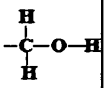
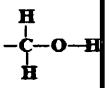
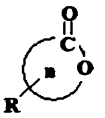
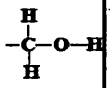
Membrane-Fouling and Cleaning State	Wavenumber				
	1667 cm^{-1} Carbonyl 	1280 cm^{-1} "Aromatic sulphone" 	850 cm^{-1} Aromatic sulphone	780 cm^{-1} Aromatic sulphone	720 cm^{-1} Aromatic sulphone
PES-Virgin	0.64	0.73	0.68	0.3	0.51
PES-1 x fouled	0.55	0.66	0.57	0.23	0.41
PES- 1f/1c-U 11	0.35	0.51	0.46	0.17	0.34
PES- 2f/1c-U11	0.42	0.53	0.38	0.15	0.31
PES- 2f/2c-U11	0.41	0.54	0.48	0.15	0.33
PES- 14f/14c-U11	0.24	0.4	0.36	0.13	0.26

Table 4.5(a/b): Averaged peak-heights of RC fouled and NaOH/Ultrasil 11 cleaned membranes. (AG-HS = Alkyl Group – Hyroxy substituted)

Membrane-Fouling and Cleaning State	Wavenumber 1725 cm^{-1} Ester 	Wavenumber 1350 cm^{-1} AG-HS 	Wavenumber 1220 cm^{-1} AG-HS 	Membrane Fouling and Cleaning State	Wavenumber 1725 cm^{-1} Ester 	Wavenumber 1350 cm^{-1} AG-HS 	Wavenumber 1220 cm^{-1} AG-HS 
RC-Virgin	0.64	0.47	0.74	RC-Virgin	0.66	0.48	0.75
RC-1 x fouled	0.58	0.33	0.62	RC-1 x fouled	0.67	0.4	0.68
RC- 1f/1c-NaOH	0.32	0.26	0.45	RC-1f/1c-U11	0.45	0.28	0.6
RC- 2f/1c-NaOH	0.27	0.22	0.38	RC- 2f/1c-U11	0.49	0.32	0.57
RC- 2f/2c-NaOH	0.21	0.23	0.34	RC- 2f/2c-U11	0.25	0.22	0.35
RC-30f/30c-NaOH	0.05	0.17	0.06	RC-25f/25c-U11	0.09	0.21	0.09

The peaks picked out for analysis in Table 4.4 and 4.5 (a/b) represents typical functional groups of the polymers for PES and RC membrane. It can also be said that these peaks are related to the functional groups with a high probability and do not interfere with other functional groups. This is particular true for the aromatic sulphone in the PES membrane polymer found.

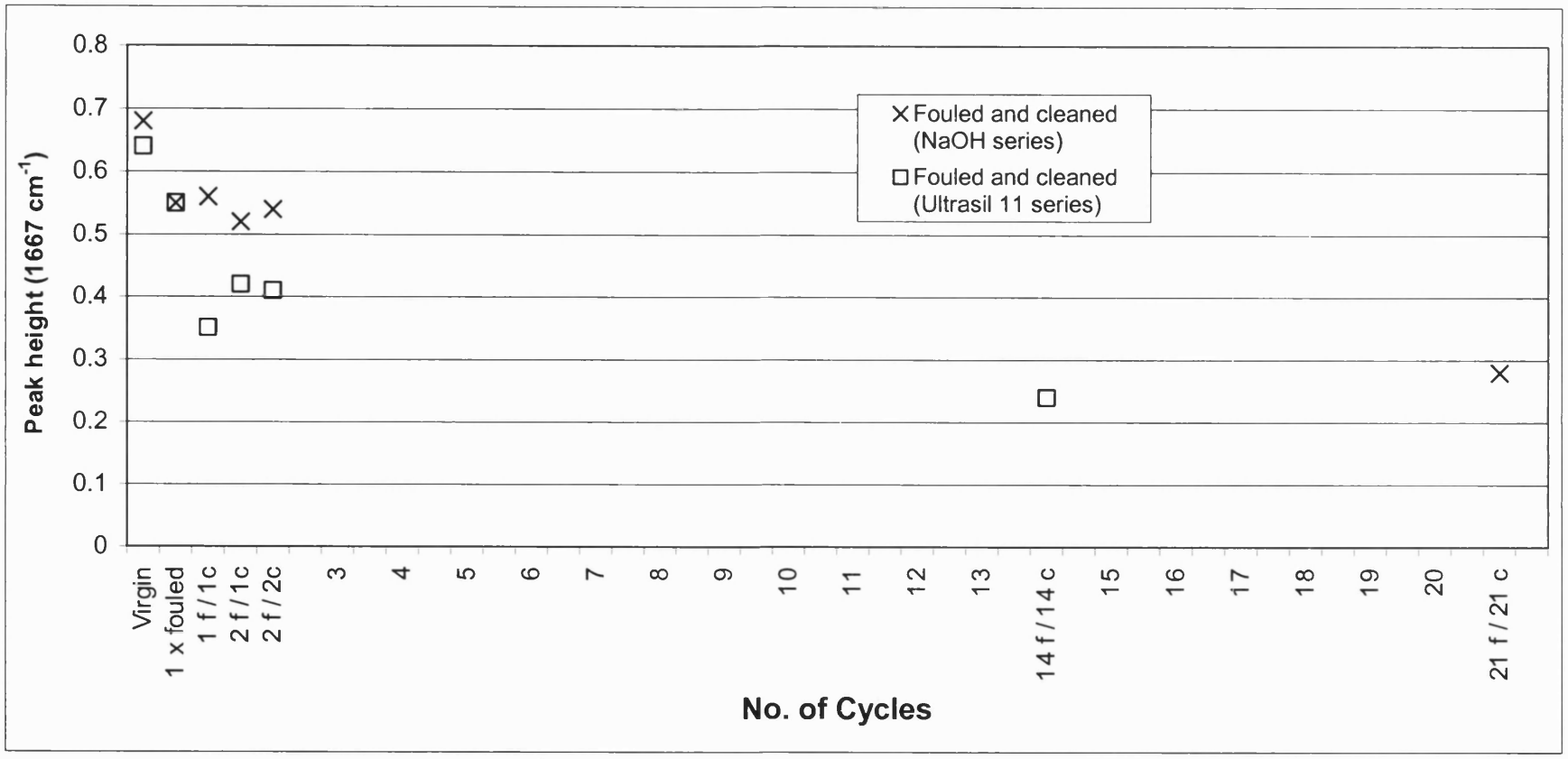


Figure 4.17: Changes of peak height (1667 cm^{-1};Carbonyl) of virgin and fouled and NaOH/Ultrasil 11 cleaned PES membrane at different stages/cycle.

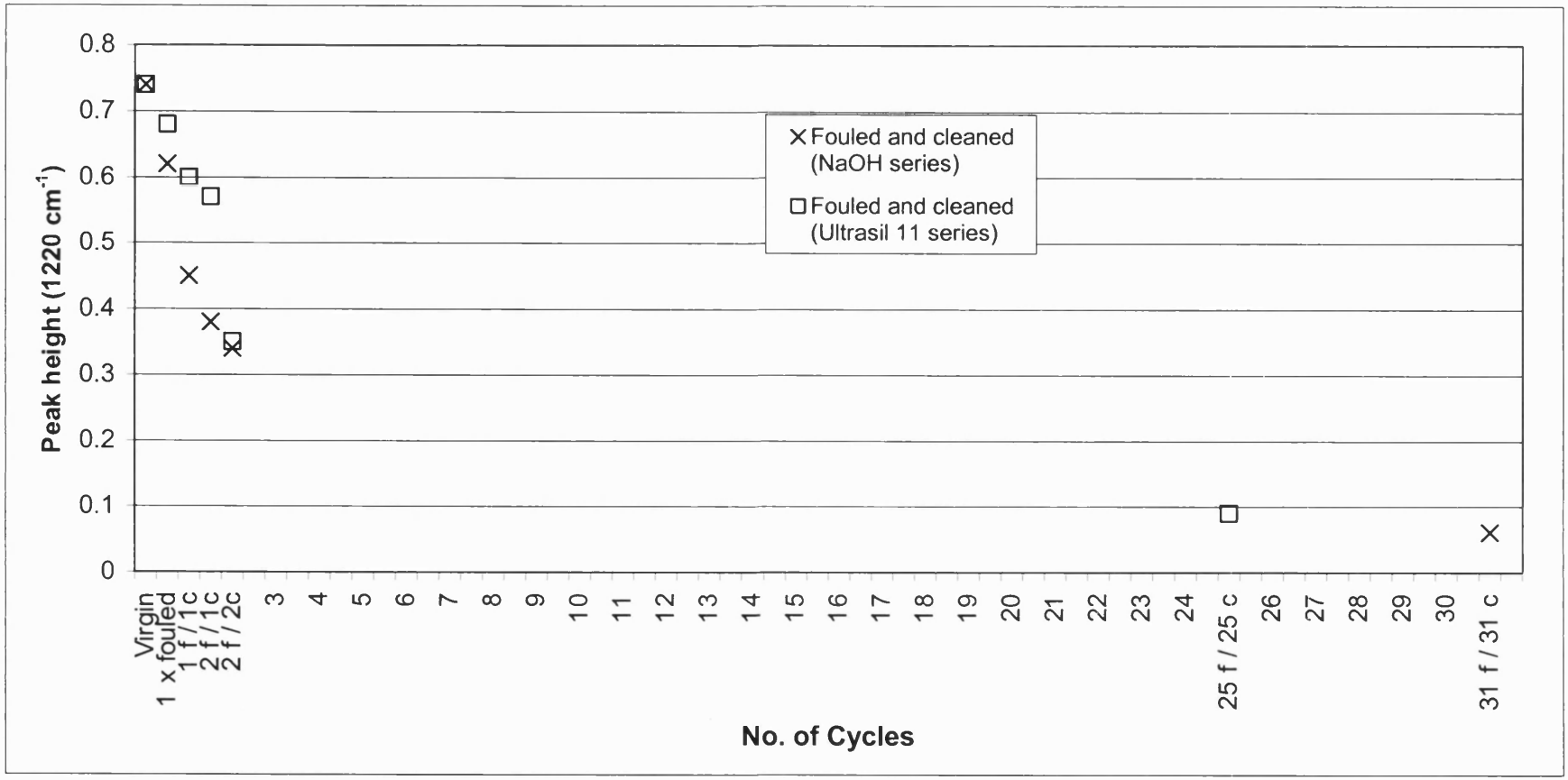


Figure 4.18: Changes of peak height (1220 cm^{-1}; Alkyl group – hydroxy substituted) of virgin and fouled and NaOH/Ultrasil 11 cleaned RC membrane at different stages/cycle.

The results for both membranes and both cleaning solutions give good information about the interaction between membrane material foulants and cleaning solution. For PES membrane when cleaned with sodium hydroxide a significant drop in peak height appears when fouled for the first time. The first cleaning with NaOH leads to a small recovery back to the virgin membrane peak height. With the second fouling step the height drops again below the value of the first fouling. When cleaned a second time the value recovers again but not above the value of the first cleaning. So, the trend is up and down with margins getting smaller and smaller towards progressing cycles until a quasi steady state is reached.

When PES membrane is cleaned with *Ultrasil 11* again, a significant drop in peak height appears when fouled for the first time. But in contrast with sodium hydroxide cleaning, the value does not recover when cleaned. The value drops significantly lower, which indicates further fouling. This further drop must be caused by the surfactants in Ultrasil 11, which becomes irreversibly adsorbed on the membrane surface, hence masking fouling. This drop happens again when cleaning for the second time is carried out but then on a much smaller scale.

Looking at the final values for both NaOH and *Ultrasil 11* cleaning, it is possible to conclude that cleaning with *Ultrasil 11* leaves a bigger fouling layer behind in comparison with NaOH cleaning. This is probably not true and occurs due to the additional surfactants adsorbing on the membrane when cleaned with *Ultrasil 11.*

When RC membrane is cleaned it does not make any difference to the spectra whether the membrane is cleaned with NaOH or *Ultrasil 11.* Both cleaning agents show the same decline. There is no improvement at all when cleaning with NaOH or *Ultrasil 11.* Interestingly, cleaning seems to make fouling worse, since it just keeps on going down. A steady state is achieved after about 10 cycles, which corresponds to the product and pure water flux measurements. This suggests that FTIR is indeed a good tool to monitor and predict fouling and cleaning behaviour. A further strong indication that NaOH and *Ultrasil 11* do not perform differently on the very hydrophilic RC membranes is the fact that the final values after 25 and 30 cycles fit exactly to the trendline and degree of decline at this number of

cycles. If *Ultrasil 11* did perform differently, one would be more likely to see a picture similar to that in Figure 5.17 for the PES membrane at high numbers of cycles.

4.4 Zeta-potential measurements

Zeta-potential is another tool for retrieving more information on the surface chemistry when membrane surfaces are fouled and cleaned. The values will provide information on the foulant/cleaner interaction.

As for the FTIR measurements the samples prepared for the fouling and cleaning step until the second cycle (2x fouled and 2x cleaned) for each membrane and cleaning solution were used. These samples along with those resulting from the long-term experiments, should give complementary information on events occurring during the most crucial start time of the process in relation to the state of the membrane after many cycles.

Zeta-potential values obtained from PES and PSf membranes when protocol 1 was applied are displayed in Tables 4.6-4.7. Following the tables the values are displayed as graphs, which provide an insight into how the zeta-potential changes with pH and how the total values of zeta-potential change with stage of fouling and cleaning.

Table 4.6: Zeta-potential values of virgin and VHV-S fouled and NaOH/Ultrasil 11 cleaned PES membranes (Protocol 1). Because r^2 >99% for streaming potential versus pressure the StDev=0.5 (n=3).

	PES-virgin	PES-1x fouled	PES-1f/1c-NaOH	PES-1-1-Ultrasil	PES-15f/15c-NaOH	PES-21-21-Ultrasil
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
7.10	-0.79	-8.02	-5.07	-7.3	-8.51	-9.5
6.30	-0.68	-8.19	-4.81	-7	-8.08	-8.6
5.50	-0.91	-7.71	-4.5	-6.57	-7.46	-8.75
4.90	-0.58	-7.73	-4.48	-6.7	-7.59	-8.58
4.40	-0.58	-7.68	-4.24	-6.79	-7.68	-8.71
3.80	-0.63	-7.79	-4.2	-7.21	-7.78	-8.88

Table 4.7: Zeta-potential values of virgin and VHV-S fouled and NaOH/Ultrasil 11 cleaned PSf membranes (Protocol 1). Because r^2 >99% for streaming potential versus pressure the StDev=0.5 (n=3).

	PSf-virgin	PSf-1x fouled	PSf-1f/1c NaOH	PSf-1f/1c Ultrasil	PSf-15f/15c-NaOH	PSf-21f/21c-Ultrasil
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
7.10	-4.95	-10.28	-9.03	-9.11	-11.81	-11.14
6.30	-3.05	-9.87	-8.92	-8.87	-11	-10.76
5.50	-2.41	-10.06	-8.61	-8.61	-10.63	-10.61
4.90	-2.01	-9.45	-8.72	-8.63	-11.09	-10.90
4.40	-1.47	-9.79	-8.72	-9.16	-10.4	-10.89
3.80	-1.06	-11.03	-9.43	-9.5	-11.8	-11.40

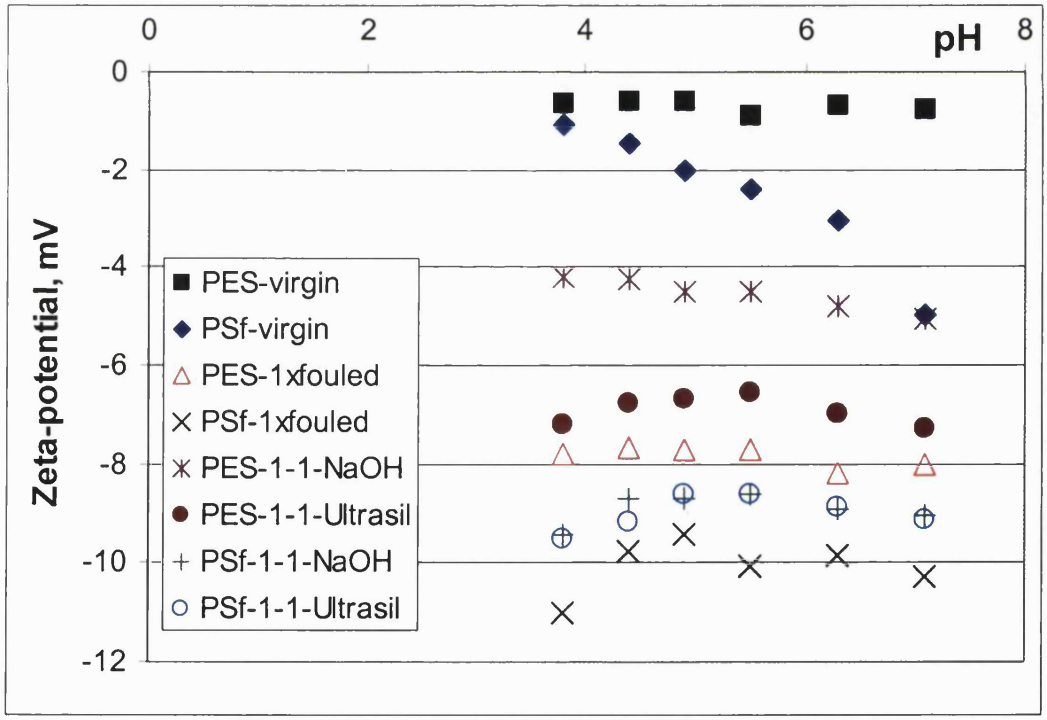


Figure 4.19: Zeta-potential values of virgin and VHV-S fouled and NaOH/Ultrasil 11 cleaned PES/PSf membranes. Corresponds to Table 4.6 and 4.7.

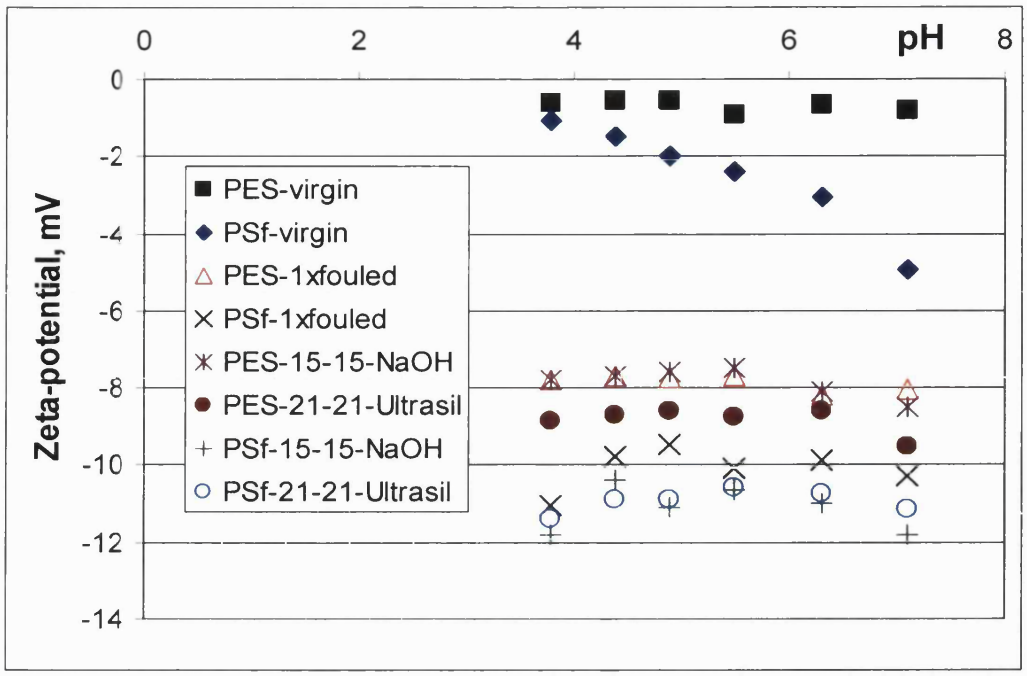


Figure 4.20: Zeta-potential values of virgin and VHV-S fouled and NaOH/Ultrasil 11 cleaned PES/PSf membranes. Corresponds to tables 5.5 and 5.6.

In Figure 4.19 one can see the zeta-potential of the virgin PES and PSf membrane. The zeta-potential for virgin PES membrane is around -0.65 when conditioned after protocol 1. When the glycerine is completely removed this value is lowered to –1.3 mV. It seems as if glycerine is shielding most of the negative charges of the membrane surface. If the membranes are fouled the influence of the polymer disappears and the zeta-potential completely changes. According o *Kontturi 1987*, the charge for lignosulphonates should sharply decline from pH 1 to pH 3,then level out at pH 7 only to decrease sharply again between pH 7 to pH 12. The graphs display only the values between pH 4 and 7.5, so the areas of sharp decreases can not be seen. Measurements above pH 7 are troublesome since alkaline conditions erode the silver coating of the electrodes. Below pH 3 the accumulation of H^+ ions was so huge that it disturbed the function of the electrodes as well. Therefore, measurements above pH 7 and below pH 3 were not carried out. The values displayed in Figure 4.19 for PES 1f/1c-NaOH represent best the decline between pH 3 and pH 7.5. For a once fouled PES membrane the

value is around –8.0 mV, for a once fouled PSf it's –10.0, which could indicates that the PES membrane resists fouling more than the PSf membrane.

If the PES membrane is cleaned with NaOH, the value is approximately cut by half to 4.5, which is partly due to removal of foulants but also probably due to attachment of Na^+-ions to the negative functional groups. If the PES membrane is cleaned with *Ultrasil 11* the value remains close to that of the once fouled membrane (-8.0 mV), which is most likely due to the attachment of anionic surfactants, but definitely also due to the work of EDTA, which removes Ca or other di- or tri valent ions from the fouling layer. That means a removal of foulants is superimposed by the attachment of surfactants and sequesteing of EDTA, hence the potential remains very negative. For long term cleaning of PES membrane with NaOH or *Ultrasil 11,* the results correspond to those results for once only cleaning, which means less negative values for NaOH and more negative values for *Ultrasil 11* cleaning.

When PSf membrane is cleaned with either NaOH or *Ultrasil 11*, it does not seem to have an effect upon the zeta potential values obtained. It appears that due to the lower surface area of the PSf membrane in comparison with the PES membrane, the attachment of surfactant plays an insignificant role. As we will see for the results obtained when membranes are cleaned according to protocol 2, these results are in agreement with the trend that the more hydrophilic the membrane the less the impact of cleaning agent and specific ingredients upon performance.

Table 4.8(a):Zeta-potential values of virgin and VHV-S fouled and NaOH cleaned PES membranes (Protocol 2). Because r^2 >99% for streaming potential versus pressure the StDev=0.3 (n=3).

	PES-virgin	PES 1x fouled	PES 1f1c NaOH	PES 2f1c NaOH	PES 2f2c NaOH	PES 20f/20c NaOH
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
3.70	-1.66	-4.92	-3.28	-11.27	-3.87	-7.56
4.70	-1.16	-6.49	-4.48	-9.96	-5.45	-7.75
5.60	-1.13	-9.42	-5.17	-9.36	-5.22	-8.07
7.00	-1.33	-9.05	-5.92	-11.62	-6.79	-7.57

Table 4.8(b): Zeta-potential values of virgin and VHV-S fouled and Ultrasil 11 cleaned PES membranes (Protocol 2). Because r^2 >99% for streaming potential versus pressure the StDev=0.3 (n=3).

	PES-virgin	PES 1x	PES 1f1c U11	PES 2f1c U11	PES 2f2c U11	PES 14f/14c U11
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
3.70	-1.66	-4.92	-7.07	-8.51	-8.64	-12.93
4.70	-1.16	-6.49	-6.13	-7.78	-7.17	-9.58
5.60	-1.13	-9.42	-5.95	-6.96	-7.39	-9.26
7.00	-1.33	-9.05	-7.24	-8.09	-7.68	-10.40

Table 4.9(a): Zeta-potential values of virgin and VHV-S fouled and NaOH cleaned RC membranes. Because r^2 >99% for streaming potential versus pressure the StDev=0.08 (n=3).

	RC-virgin	RC 1x fouled	RC 1f1c NaOH	RC 2f1c NaOH	RC 2f2c NaOH	RC 30f/30c NaOH
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
3.70	-0.94	-1.60	-1.19	-1.33	-1.43	-1.75
4.70	-1.04	-1.59	-1.48	-1.75	-1.56	-2.09
5.60	-1.08	-1.69	-1.64	-1.77	-1.71	-2.28
7.00	-1.14	-1.69	-1.81	-1.92	-1.77	-2.40

Table 4.9(b): Zeta-potential values of virgin and VHV-S fouled and Ultrasil 11 cleaned RC membranes. Because r^2 >99% for streaming potential versus pressure the StDev=0.05 (n=3).

	RC-virgin	RC 1x	RC 1f1c U11	RC 2f1c U11	RC 2f2c U11	RC 25f/25c U11
pH	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]	ζ [mV]
3.70	-0.94	-1.60	-1.15	-1.25	-1.26	-2.02
4.70	-1.04	-1.59	-1.52	-1.69	-1.54	-2.18
5.60	-1.08	-1.69	-1.72	-1.79	-1.72	-2.24
7.00	-1.14	-1.69	-1.93	-1.98	-1.88	-2.37

The zeta potential results obtained when cleaning after conditioning according to protocol 2 are more reliable than the results for cleaning after protocol 1, simply because glycerine is completely removed and cleaning is carried out at high temperatures. High cleaning temperatures will support removal of foulants and also support the attachment of surfactants on the membrane. Therefore, differences in cleaning behaviour should result in bigger differences in zeta-potential and trends should be seen more easily. However, looking at the result for PES membrane for both sets of results, one can see that the results are very similar to cleaning according to protocol 1 and lie within the standard deviation.

The results for protocol 2 are displayed in tables 4.8(a/b) and 4.9(a/b). It was interesting to follow the development of the zeta-potential over the different stages of fouling and cleaning. This can be done when picking out the zeta-potential for one pH (e.g. pH 3.7). This is normally not valid to do this, as the zeta-potential is dependent on pH. But as one can see from the values in the tables, fouling and cleaning has the same impact on zeta-potential at all pH's, hence fouling and cleaning is shifting the zeta-potential for all pH's to the same degree. Variations lie within the standard deviation.

Cleaning with NaOH and *Ultrasil 11* follows different patterns for PES membranes. The results do confirm that what was already described for the FTIR results. When cleaned with sodium hydroxide, the value returns closer to that of

the virgin membrane. When fouled again, the value drops below the one of the once fouled membrane only to return again when cleaned. The same is valid for the cleaning mechanism as was said for the zeta potential results discussed for protocol 1. For *Ultrasil 11* cleaning the picture is very different. At pH 3.7 the values keep on dropping no matter if fouled or cleaned. As for the FTIR results, it clearly indicates that another phenomenon is occurring, most likely the attachment of surfactants and in addition the work of EDTA. It should be noted that the values at other pH's give a slightly different picture. But in general, the recovery of zeta-potential when cleaning with *Ultrasil 11 is* not as big as that seen when cleaning with NaOH. That *Ultrasil 11* has a different impact can also be seen in the results after many cycles. For *Ultrasil 11* the zeta potential value is much more negative than it was in the case for NaOH cleaning, which further supports the explanation that surfactants are adsorbing on the membrane fouling layer surface.

For RC membrane the results are rather different but in comparison to the much more hydrophobic PES membrane highly interesting. When fouled once, the zeta-potential drops quite significantly to almost double the negative value of that recorded for a virgin membrane. Together with the FTIR results, this suggests that very hydrophilic membranes do also foul to a certain degree, but less than hydrophobic membranes. Then, when cleaned something interesting happens. It seems that during the first cycle cleaning has no impact whatsoever, when looking at the results at pH 3.7. But for the other pH values there is a very small impact of cleaning detected. When the RC membrane becomes more fouled after a greater number of cycles, the surface becomes more attractive for the adsorption of surfactants. This explains why with increasing numbers of cycles the zeta-potential is more negative after *Ultrasil 11* cleaning in comparison to NaOH cleaning.

Chapter 5

Results

and

Discussion

Part II

Filtration Data

5 Introduction

This chapter will show the core results of this study. They will be grouped according to certain aspects in terms of the parameter under investigation and described both quantitatively and qualitatively, in terms of fouling material analysis, impact of cleaning agents and membrane material on performance over short and long term.

5.1 Performance of filtration (cold wash)

Initial results present the filtration data. This is necessary in order to understand all other related data, which are taken from different stages of the filtration process. The graphs presented on the following pages are obtained with the protocol developed in the first stages of this study (see Appendix for protocol details). To remind the reader; the conditioning step (removing glycerine) was incomplete and cleaning was carried out at ambient temperatures. Nevertheless, the results are still worthwhile presenting, since incomplete conditioning is common practise in industry and the results for "cold washes" are interesting as well in particular in comparison with results for "hot washes".

Figure 5.1(a) shows the product flux recoveries after sodium hydroxide cleaning of a PES membrane. The problem is that all the data acquired during the filtration tests are hard to display in one graph. So, for the sake of understanding and interpreting the data, compromises were made and flux data during the decline period was to be left out. In the case of displaying product fluxes only the initial and final flux values are displayed. Those values are measured after the first 5 minutes of the filtration and 5 minutes before the filtration was stopped.

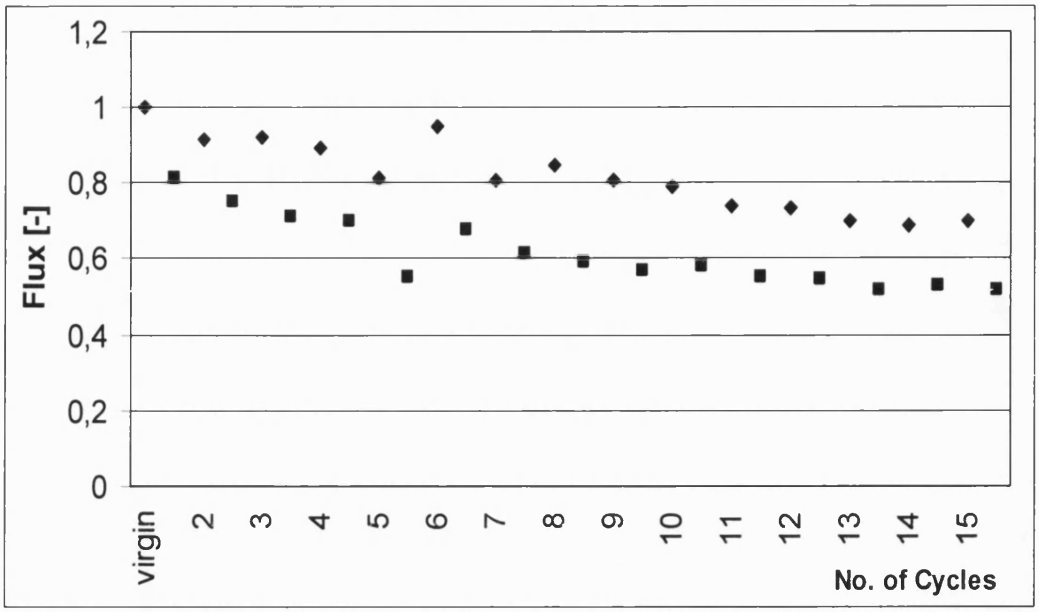


Figure 5.1(a): Product flux development after NaOH cleaning of VHV-S fouled PES membrane (0.5wt%, 22°C, 1.9 ms^{-1}) ◆ *start value;* ■ *final value.*

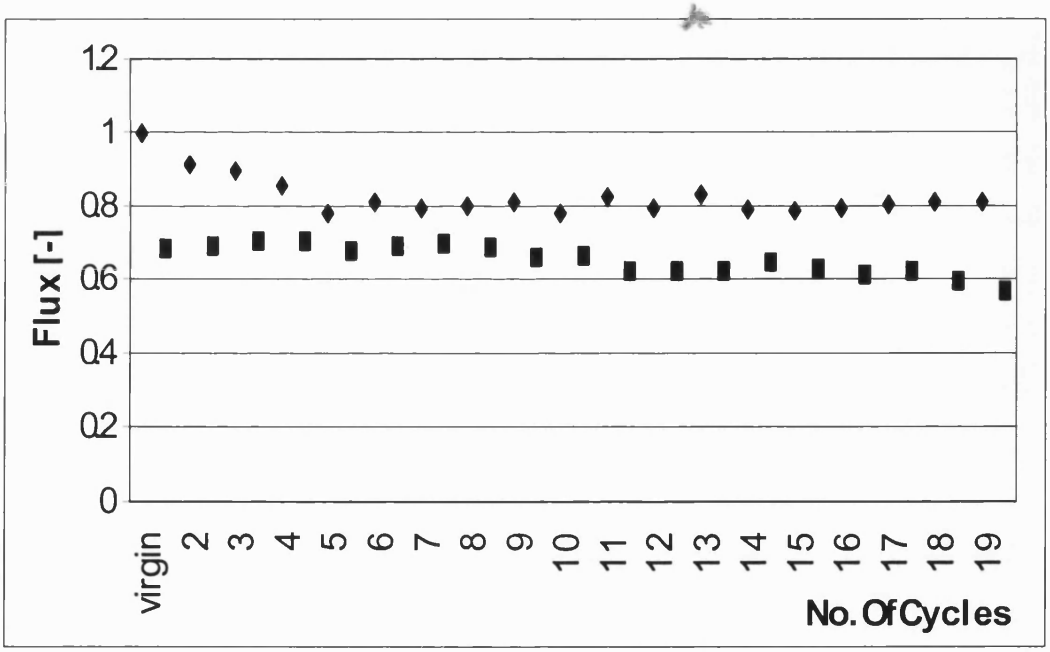


Figure 5.1(b): Product flux development after Ultrasil 11 cleaning of VHV-S fouled PES membrane (0.5wt%, 22°C, 1.9 ms^{-1}). ◆ *start value;* ■ *final value.*

Whilst the final value was always very stable, the values in the beginning fluctuated a lot, probably due to pressure, flow and temperature variations across the module and thus the steady-state value is of more interest. As already stated, a gel layer is developed, which determines the filtration performance after the steady-state is reached and the further decline is very small even over long periods of time (see Figure 5.5). Therefore, these final values are crucial, and all other data can be neglected. However, for the sake of completeness at least the starting values of the cycles are displayed.

In Figure 5.1(a) the product flux final values for cleaning with NaOH show a decline over the first 7 cycles to reach a quasi steady state. This decline is likely due to the presence of sodium ions, which neutralise the charges on the lignosulphonates, and make the surface more hydrophobic, hence subsequently more attractive for additional hydrophobic foulants. This can be concluded from the zeta-potential results discussed in part I of the result chapter as well. Interesting is, that after 7 cycles a quasi steady state is reached and it raises the question why there is no further decline. Surface analysis, such as zeta-potential measurements, force measurements with AFM (*Chukwuemeka* 2002) and contact angles suggest that the pristine membrane surface gets covered more and more by the foulants, until the membrane material has no further influence on further foulant precipitation. The fouling layer becomes dominant over the membrane surface material. It is interesting that a once fouled membrane has almost the same zeta-potential value as one where the flux has reached a steady state.

The driving force for amphiphilic molecules, such as the fouling material, to adsorb on interfaces is the lowering of free energy of that phase boundary. The amphiphilic foulants adsorb with their hydrophobic moiety on the hydrophobic surface, in order to remove these hydrophobic groups from contact with water and lower the free energy of the system. This explanation was used also by *Ruohomäki et al* 1998 for humic acid adsorption. This process of adsorption will occur until the fouling layer is densely packed. An equilibrium on the surface is established when the attachment of the hydrophilic head group toward the water equals that of the hydrophobic moiety towards the surface.

Figure 5.1(b) deals with the development of product fluxes when cleaned with *Ultrasil 11*. There is no decline over the first 7 cycles as was found for NaOH cleaning. A quasi steady state is already reached after the first cycle, with only a very small decline over the long term. The reason for this is that, *Ultrasil 11* contains EDTA, a sequestrant for cations, in particular for those with double charges, like Ca^{2+} or Mg^{2+}. Therefore, the negative functional groups of the foulants are maintained negative, and hence more hydrophilic, *Hong and Elimelech* 1997. In addition, *Ultrasil 11* contains anionic and nonionic surfactants. Both will attach on hydrophobic surfaces (see Chapter 2) and increase hydrophilicity. For every subsequent fouling cycle, further attachment of surfactants is lowered such that it almost becomes negligible. Hence, very small flux declines are observed over the long term. The zeta-potential values confirm the flux results. Values of a single fouled membrane do not differ very much from a once-fouled and once-cleaned membrane, and neither do they vary much from a multiple fouled membrane. The differences in the values fall within the standard deviation range and are therefore not significant. Cleaning is changing the surface energy in such a way that equilibrium is already established after the first cycle.

For process considerations it should be pointed out that cleaning with sodium hydroxide provides a better performance than with *Ultrasil 11* over the first 7 cycles. This suggests that over the short term NaOH could be used, before changing to another cleaner, such as *Ultrasil 11*.

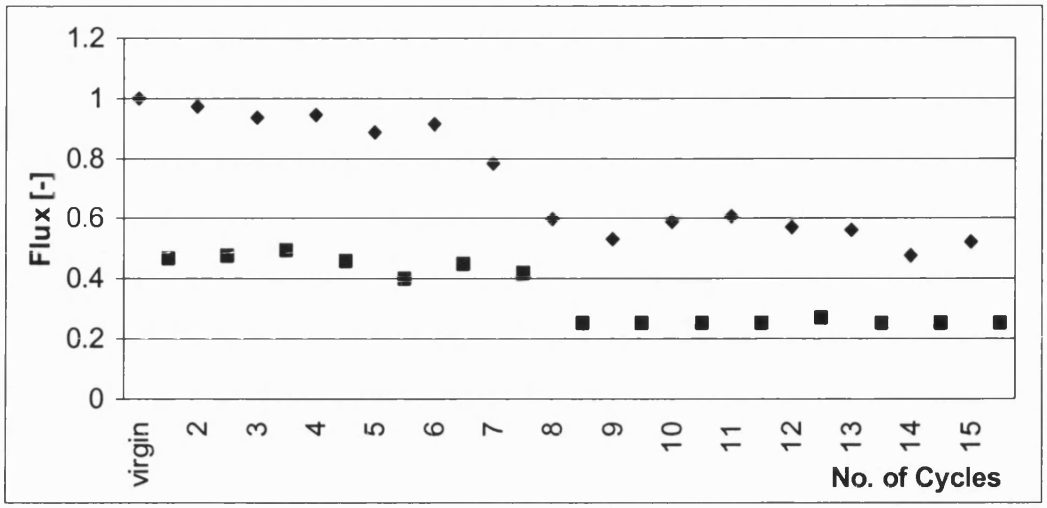


Figure 5.2(a): Product flux development after NaOH cleaning of VHV-S fouled PSf membrane (0.5wt%, 22°C, 1.9 ms^{-1}). ◆ start value; ◆ start value; ■ final value.

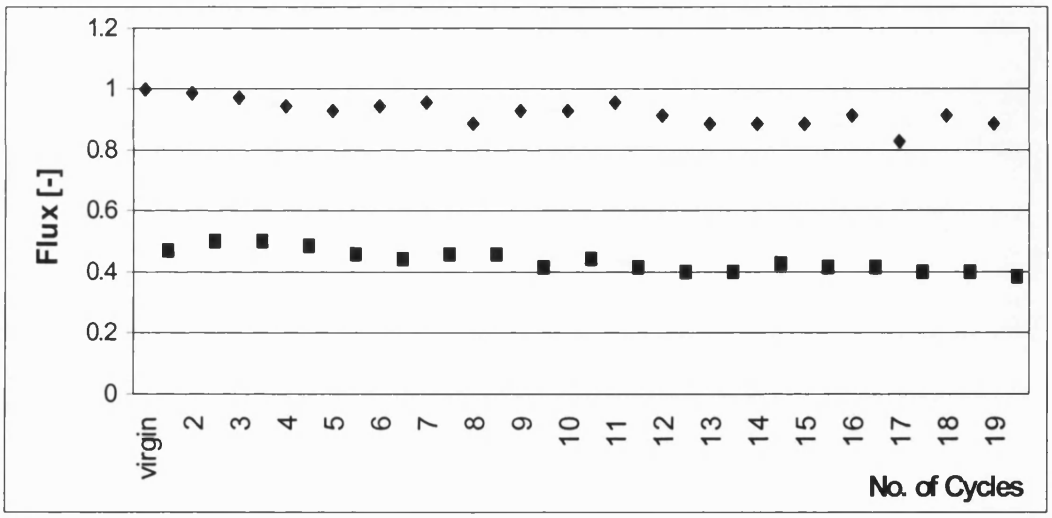


Figure 5.2(b): Product flux development after Ultrasil 11 cleaning of VHV-S fouled PSf membrane (0.5wt%, 22°C, 1.9 ms^{-1}). ◆ start value; ■ final value.

Figure 5.2(a) shows the product flux development after sodium hydroxide cleaning of a PSf membrane. Unlike the PES membrane there is almost no flux decline over the first 6 cycles. After the 6th cycle the flux dramatically drops to settle for a flux of 20% of the virgin membrane. The zeta-potential measurements show no change between once fouled and once fouled and cleaned membrane, which indicates that there is actually no chemical modification of the surface-

fouling layer on the membrane. The cleaning depends entirely on physically removing the gel layer, and after the 6th cycle it appears that almost a complete pore blocking occurs. It is uncertain why no chemical modification has taken place. Atomic force pictures reveal that PSf has a lower number of pores/unit area than PES, *Chukwuemeka* 2002. The pore entrances of PSf are bigger than for PES and less numerous. Therefore, the surface area in total for PES is much bigger than it is for PSf. Hence, interactions between foulant and membrane material are more likely to happen for the PES than for the PSf membrane. Conversely the less pores available for permeation, the more important it becomes when a single pore of those remaining pores actually gets blocked. Therefore, for PSf, the dominant force to resist flux seems to be physical blocking. Also, according to *Chukwuemeka* 2002, the roughness for PSf is higher than for the PES membrane. Roughness, according to *Bowen and Doneva* 2000, is one of the most important membrane surface properties as it has a strong influence on adhesion (fouling) and also on local mass transfer. *Vrijenhoek et al.* 2001 confirmed this suggestion by *Bowen* and goes further by saying that surface roughness is the most significant property for influencing fouling and more important than physical and chemical operating conditions. A further good explanation was brought forward by *Mietton-Peuchot and co-workers* 1997. Their study was on surfactant adsorption and explanations are closely related to the surface area explanation above in this study. They found that the larger the pore diameter in comparison to the diameter of the permeating surfactant micelles, the smaller the adsorption on pore walls. Therefore on membranes with larger pores, the adsorption phenomena and foulant or cleaning agent interaction with the membrane material is less likely to happen or happen on a longer time scale. But fouling still occurs, but is of more physical nature with blocking by particles and less due to adsorption and a change of surface chemistry.

Figure 5.2(b) shows the product flux development after *Ultrasil 11* cleaning of a PSf membrane. According to the zeta-potential value, *Ultrasil 11* is not modifying the fouling layer chemically. But the flux decline is less significant than for NaOH cleaning and a smoother decline over the long term can be seen. It suggests that ionic and nonionic surfactants get attached to the membrane and influence flux

decline. Nonionic surfactants would not contribute to the zeta-potential measurements, but greatly influence the hydrophilicity, hence maintaining the permeation at a certain level and buffering flux decline due to adsorption of further foulants.

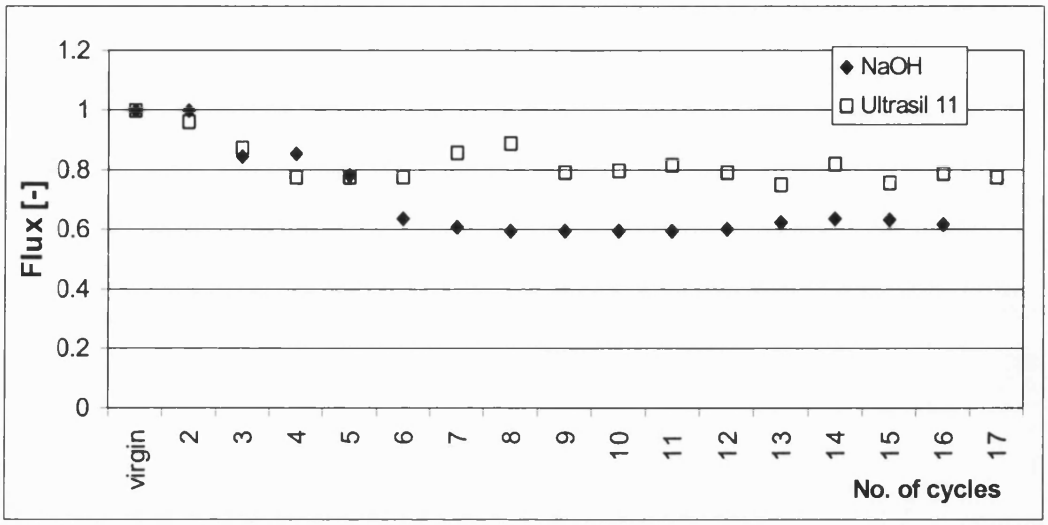


Figure 5.3(a): Pure water flux development after cleaning of VHV-S fouled PES membrane with different agents (0.5wt%, 22°C, 1.9 ms^{-1}).

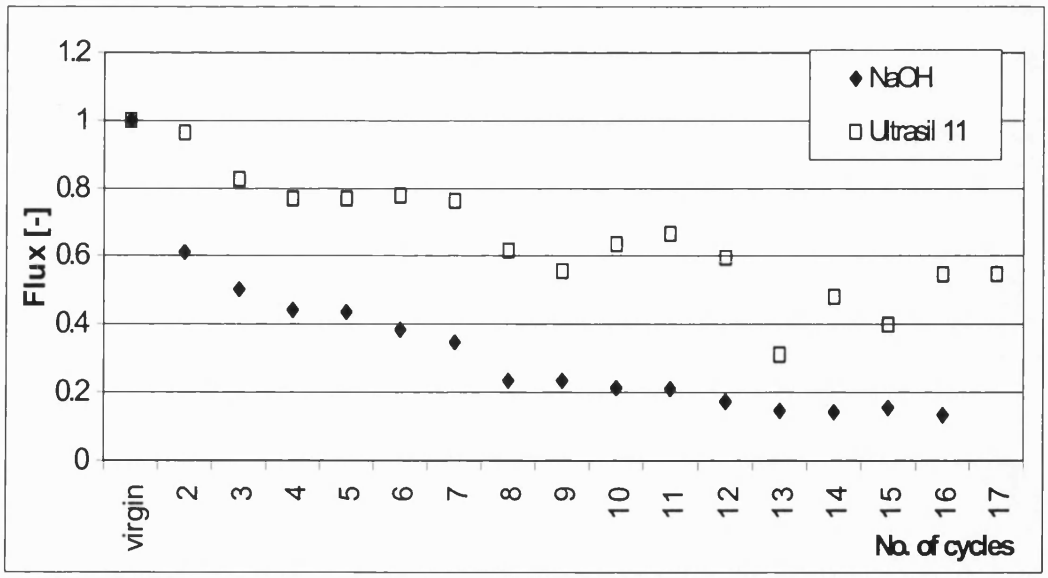


Figure 5.3(b): Pure water flux development after cleaning of VHV-S fouled PSf membrane with different agents (0.5wt%, 22°C, 1.9 ms^{-1}).

Figure 5.3(a) shows the pure water flux development after cleaning with sodium hydroxide and *Ultrasil 11* on PES membrane. The pure water fluxes are complementary to the product fluxes, since they reveal more about the fouling mechanism and chemical modification of the fouling layer than the product flux can on its own, (see Chapter 2). For PES membrane up to the 5th cycle the PWF declines rather rapidly, whether it is cleaned with NaOH or *Ultrasil 11*. After the 5th cycle the PWF, when cleaned with NaOH, drops further, whilst the PWF, when cleaned with *Ultrasil 11,* remains stable. For NaOH cleaning the PWF results are a confirmation of the product flux results. For *Ultrasil 11* cleaning it becomes obvious when the effects of different components of *Ultrasil 11* start to function with the effect of no further decline. Remarkably, the initial decline of the PWF's until the 5th cycle coincides exactly with the decline of the initial start values of product flux. The initial product flux values are measured when there is no gel layer. Therefore, the drop must be ultimately related to irreversible fouling on the membrane surface and related to real blocking. Chemical modification due to cleaning already starts during the first cycle, as zeta-potential results reveal, (see chapter 4). As a result the final fluxes keep stable showing only a very small decline over the long term.

Figure 5.3(b) shows the pure water flux development after cleaning with sodium hydroxide and *Ultrasil 11* on PSf membrane. The PWF for cleaning with NaOH clearly shows that there is a continuous decline. Unlike PES, there is no stabilisation and decline appears to be entirely due to real blocking of pores. For cleaning with *Ultrasil 11* also a continuous decline of PWF's can be observed, but on a smaller scale. The minor components of *Ultrasil 11* seem to make an impact, but as already stated above, the dominant resistance towards flow is real physical blocking rather than changing of the fouling.

5.2 Performance of filtration (hot wash)

On the following pages the filtration data obtained using the second conditioning protocol will be presented. To remind the reader, the difference to the first

protocol is that the conditioning was carried out with pure water (not *Ultrasil 11*) until glycerine was completely removed. The conditioning and subsequent cleaning cycles were carried out at 60°C.

5.2.1 Removal of glycerine

In Figure 5.4 the temperature dependency of the removal of glycerine can be seen. After 20 min. approximately 80% of the total amount of glycerine is removed from the pristine membrane. One would expect that such an amount of removal would be sufficient and that the remaining glycerine would not have any impact on fouling. But that seems not to be the case. In Figure 5.5 the effect of incomplete glycerine removal is depicted, when protocol No. 1 is used. Each point was obtained from a new membrane fouled for a different length of time. For both membranes, PES and PSf, it can be seen that for ½ and 1 hour of fouling the decline is severe. It means that remaining glycerine makes the membrane surface more hydrophilic and provides some protection against fouling.

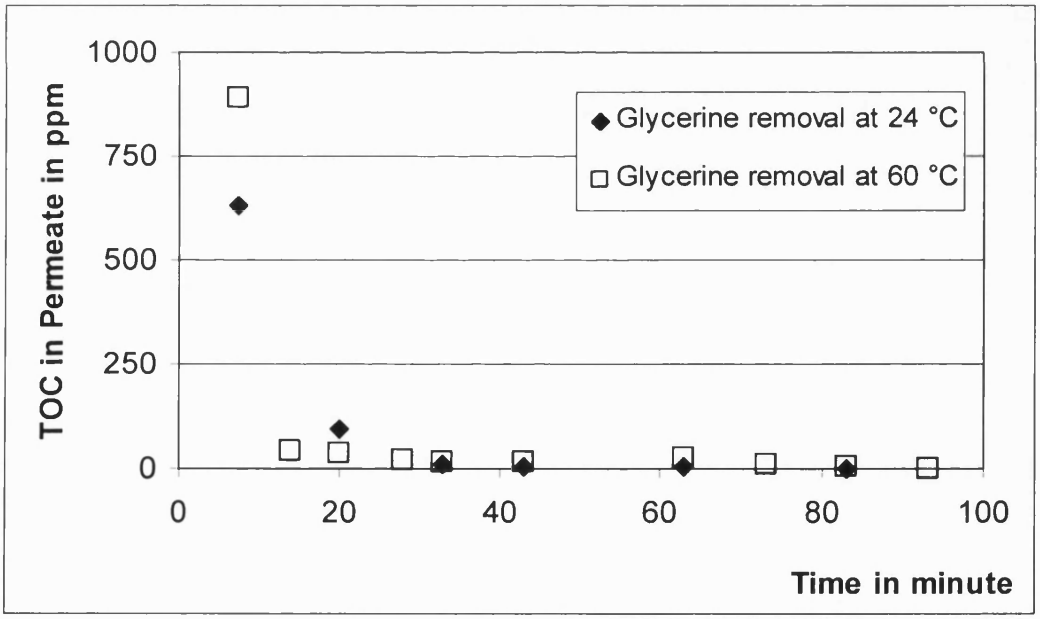


Figure 5.4: Glycerine removal on PES membrane (measured as TOC) at two different temperatures

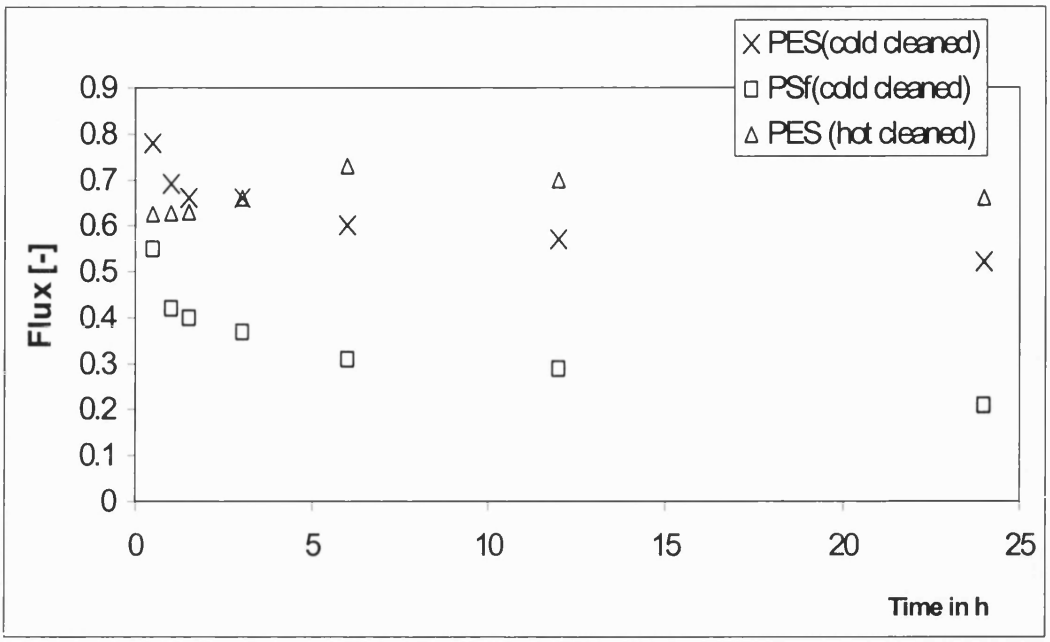


Figure 5.5: Cleanability of short and long term fouled membranes (one cycle). The membrane is fouled for a different length of time. Cold cleaned=1st protocol used (0.5wt%NaOH, 22°C, 1.9 ms-1) hot cleaned = 2nd protocol used. (0.5 wt% NaOH, 60°C, 1.9 ms-1).

In the case when the glycerine is completely removed, as it can be seen for the curve "hot cleaned", this decline cannot be seen and the membrane fouls less severely than it would have be when the glycerine is not removed completely. *Le* 1982 recorded similar results when he treated UF membranes with a polyethyleneglycole (PEG) solution. Like glycerine, PEG is hydrophilic and makes by adsorption the membrane surface more hydrophilic, hence giving the membrane some protection against fouling. Why the cleanability (Figure 5.5) increases between 1 ½ and 6 hour fouling is not exactly clear. There seems to be a clear trend already visible after ½ hour. It is possible that some reconfiguration of molecules occurs during the period mentioned. It is well known that with time small molecules are replaced by molecules with a higher molar mass along the membrane surface. But if that is really a reason for the improvement of flux recovery is of great doubt, since this improvement does not occur for the cold wash. After a fouling period of 6 hours, the trend for all three curves is the same,

which provides confidence of the reliability of the results, especially since every point was measured with a new membrane sheet with slightly different pore size distribution.

The trends seen in Figure 5.5 were used to determine the fouling time for developing the protocols. In industry, cleaning can have intervals between 24 hours and 1 week. The fouling times used in the protocols are therefore not intended to represent industrial practice. However, the fouling time of 1 ½ hours for the 1st protocol and 2 hours for the 2nd protocol was a compromise between reality and the limited time available for this study. A time of 1 ½ hours was necessary to establish the gel layer and steady state flux decline. After that crucial first 1 ½ hours, the decline is small and does not justify the additional time necessary to generate fouled membranes. In addition, it is expected that the overall trends over many cleaning cycles will be the same regardless if membranes are fouled for 2, 6 or 24 hours.

5.2.2 Filtration data

The filtration data obtained with the help of the second protocol was extended beyond the quasi steady state reached. The steady state is seen as an ideal platform to test the impact of various process parameters, such as temperature, concentration or crossflow velocity. In this study, at steady state the impact of cleaning temperature and concentration of cleaning agent was studied. When the pure water flux dropped below the steady-state value an additional cleaning was carried out to bring the value back to the steady-state value. This was necessary for having a reference value in order to make changes due to variations of cleaning parameters comparable.

5.2.2.1 Product flux

In the following figures the product flux development is diagrammed after sodium hydroxide and *Ultrasil 11* cleaning of PES and RC membranes.

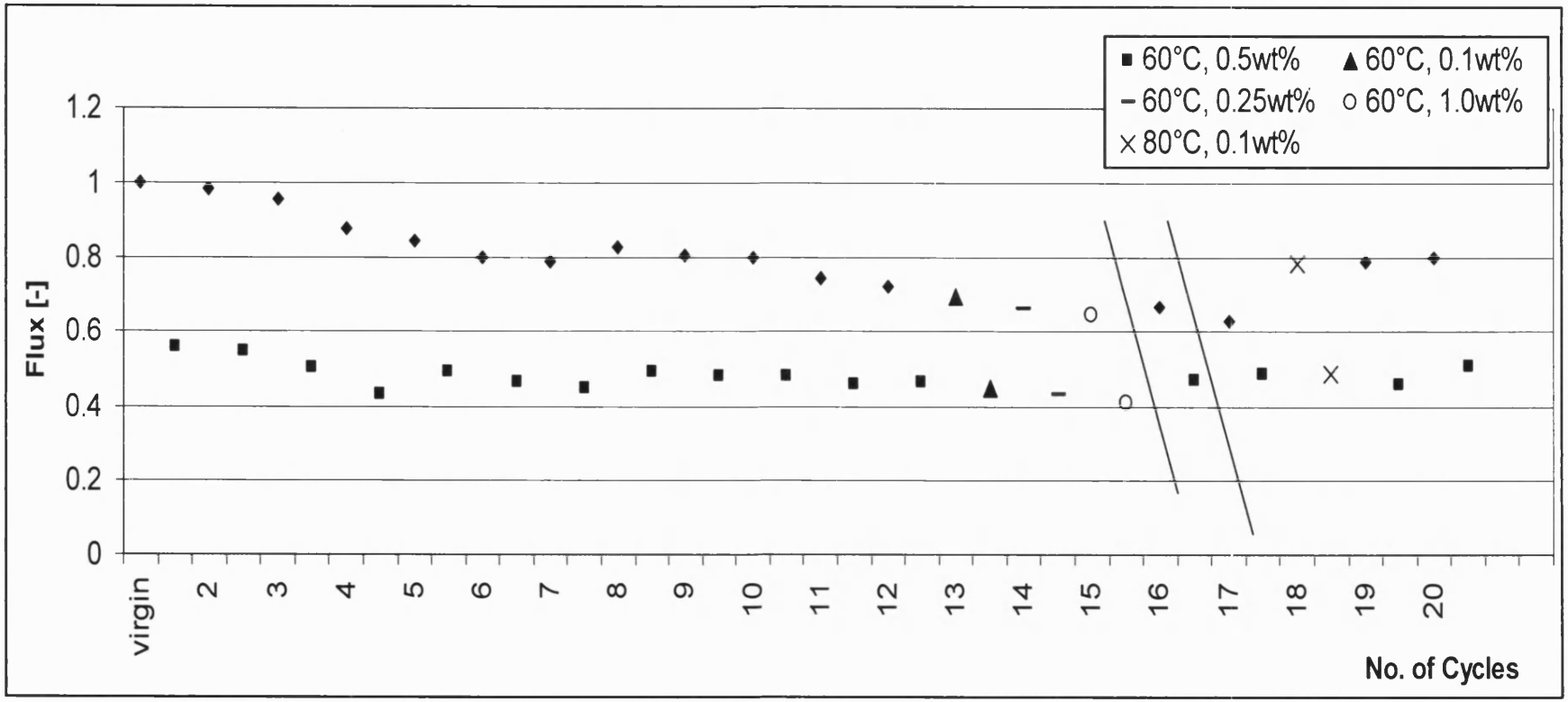


Figure 5.6(a): *Product flux developmentt after NaOH cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.5wt% NaOH, 60°C, 1.9 ms^{-1}).* ◆ *start value;* ■ *final value.*

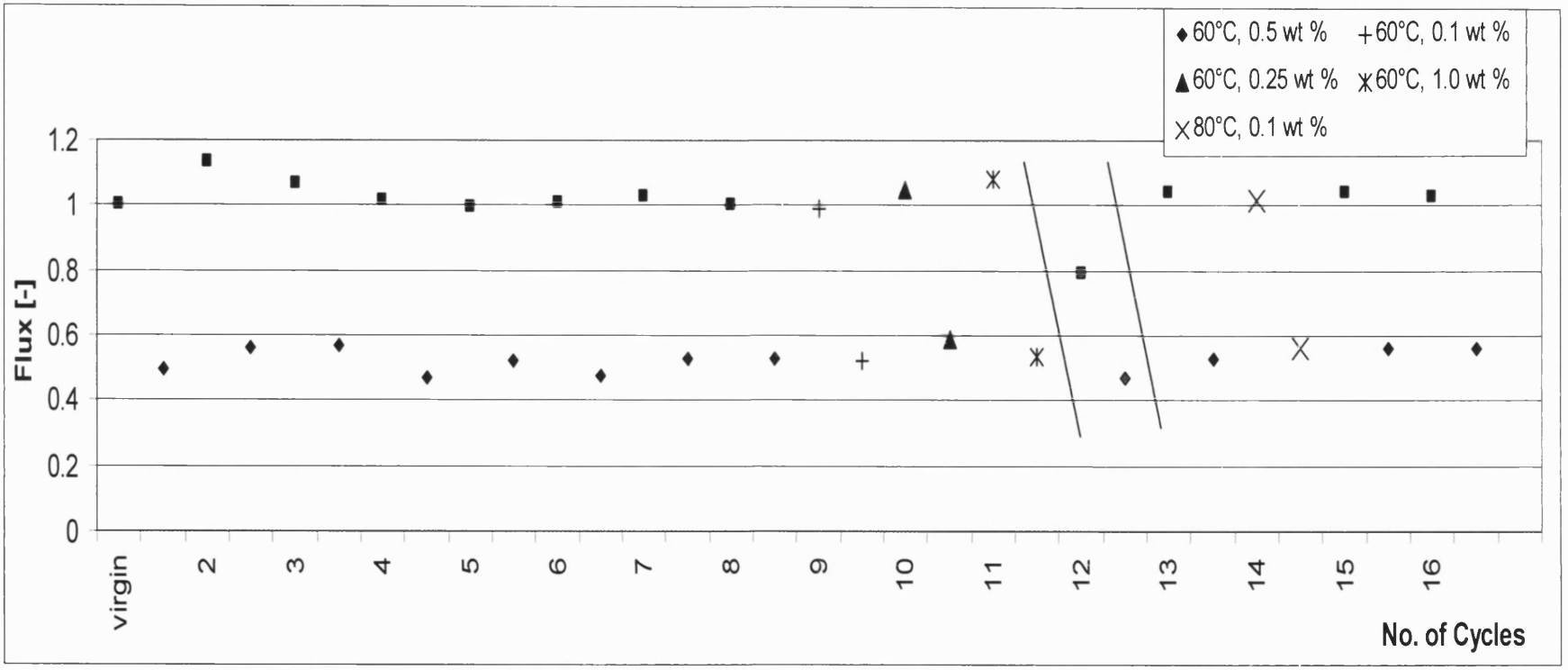


Figure 5.6(b): Product flux development after Ultrasil 11 cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.5wt% Ultrasil 11, 60°C, 1.9 ms^{-1}). ◆ start value; ■ final value.

In Figure 5.6(a) the product flux development after sodium hydroxide cleaning is depicted. The trends for hot wash (60°C) are almost the same as for cold wash (22°C). A steady-state is reached after the 7th cycle for the final values, but start values keep on declining for both, hot or cold wash, (see also Figure 5.1(a) and explanation for the trends. As expected, cold washes are not as effective as hot washes for short and long term. For cold wash the total decline when looking at the final product values from cycle 1 to cycle 7 is approximately 20%. For hot wash it is just about 10%. For both types of washes, it seems that the decline is due to a permanent build up of fouling material. This will be discussed further, when PWF and retention results are presented.

In Figure 5.6(b) the product flux development after *Ultrasil 11* cleaning is presented. Here, differences can be seen in comparison to cold washes, Figure 5.1(b). The most eye-catching difference is the product flux development of the start values. For cold wash, this was declining until cycle 7, for hot wash the flux remains constant and even shows an increase for cycle No. 2. For hot wash, the flux remains over short and long term at the flux level of the virgin membrane, which is a perfect result and represents the ideal case from the industrial point of view. However, from the scientific point of view the membrane gets fouled as well as AFM pictures and FTIR scans reveal. In fact, *Ultrasil 11* is unable to remove the foulants and return the membrane to a pristine state. *Ultrasil 11* is strongly modifying the surface of the membrane chemically, by adsorption of anionic and in particular nonionic surfactants. Also EDTA removes cations, preferentially multivalent, *Yoon et al.* 1998. The removal here results in a sudden rise in product flux at the second cycle. The chemical modification leads to an increase in hydrophilicity. That will serve as a protection for repelling hydrophobic foulants, *Cho et al.* 2000. Since there is no decline observed, fouling is minor and does not get to a degree where it reduces flux by actually blocking pores.

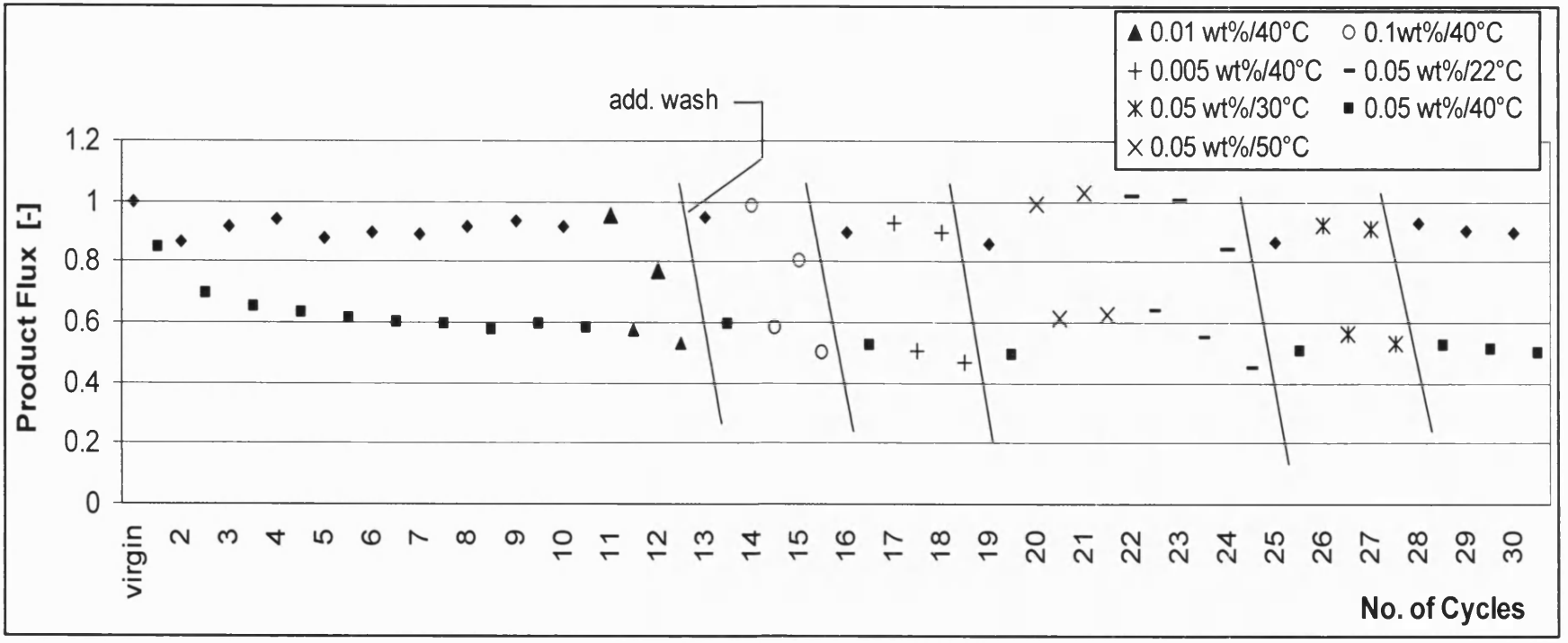


Figure 5.7(a): Product flux development after NaOH cleaning of VHV-S fouled regenerated cellulose (RC) membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% NaOH, 40°C, 1.9 ms^{-1}). ◆ *start value;* ■ *final value.*

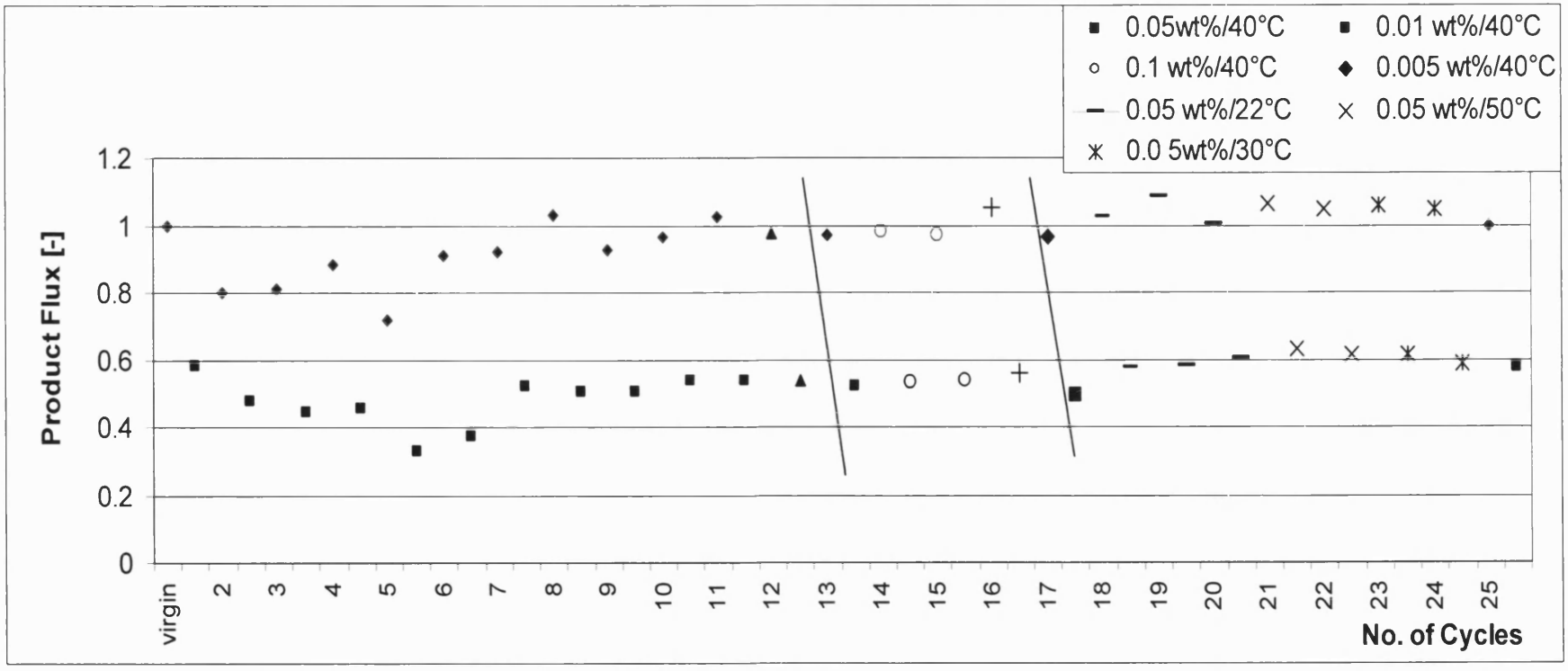


Figure 5.7(b): Product flux development after Ultrasil 11 cleaning of VHV-S fouled regenerated cellulose (RC) membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}). ◆ start value; ■ final value.

Figure 5.7(a) shows the product flux development after sodium hydroxide cleaning of a regenerated cellulose membrane. Regenerated cellulose is a very hydrophilic material, but susceptible to deterioration when unsuitable process parameters are used. According to the manufacturer the material can withstand only temperatures up to 55°C and pH's between 3 and 11. Therefore, the concentration of cleaning agent was reduced ten fold in comparison to the PES membrane, and a cleaning temperature of 40°C was used. For sodium hydroxide cleaning a steep decline was found until a steady state was reached at about the 6th cycle. The trend is almost the same when compared to PES membrane, but for RC a steady state is reached at approximately 60% of the initial flux of the virgin membrane, for PES this is ~50%. The smaller decline can be contributed certainly to the much higher hydrophilicity of the RC membrane, hence a smaller fouling tendency for hydrophobic molecules.

Figure 5.7(b) shows the product flux development after *Ultrasil 11* cleaning of a regenerated cellulose membrane. The final values of product flux decline until cycle 7. Then it starts to recover and returns almost to the value of the virgin membrane. For the start values of the product flux the recovery occurs even earlier. It declines to the third cycle, to recover then slowly until after the 11th cycle the value of the virgin membrane is re-established. With the precipitation of foulants the membrane slowly becomes more hydrophobic. With increasing hydrophobicity, the foundation is laid for adsorption of nonionic surfactants from *Ultrasil 11*. With every cycle the membrane becomes more hydrophilic again until a balance is reached between the hydrophobic foulants and surfactants. Anionic surfactants present in *Ultrasil 11* will support this process, since they attach on hydrophilic surfaces head on, leaving the hydrophobic moiety stretched into the bulk solution.

5.2.2.2 Pure water flux

In the following figures the pure water flux development is presented after NaOH and *Ultrasil 11* cleaning of PES and RC membrane.

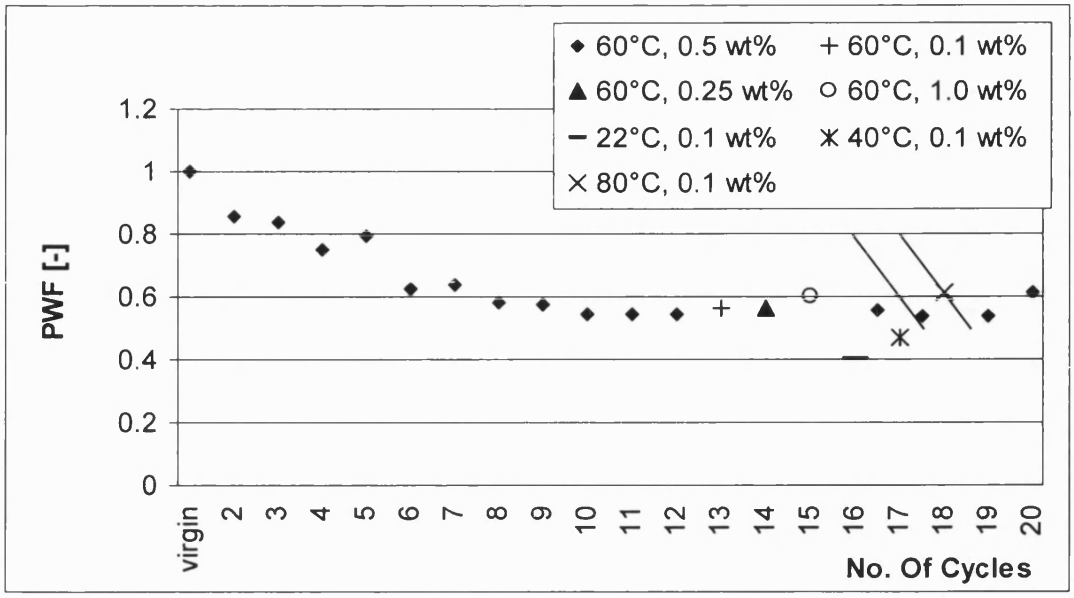


Figure 5.8(a): Pure water flux development after NaOH cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.5wt% NaOH, 60°C, 1.9 ms^{-1}).

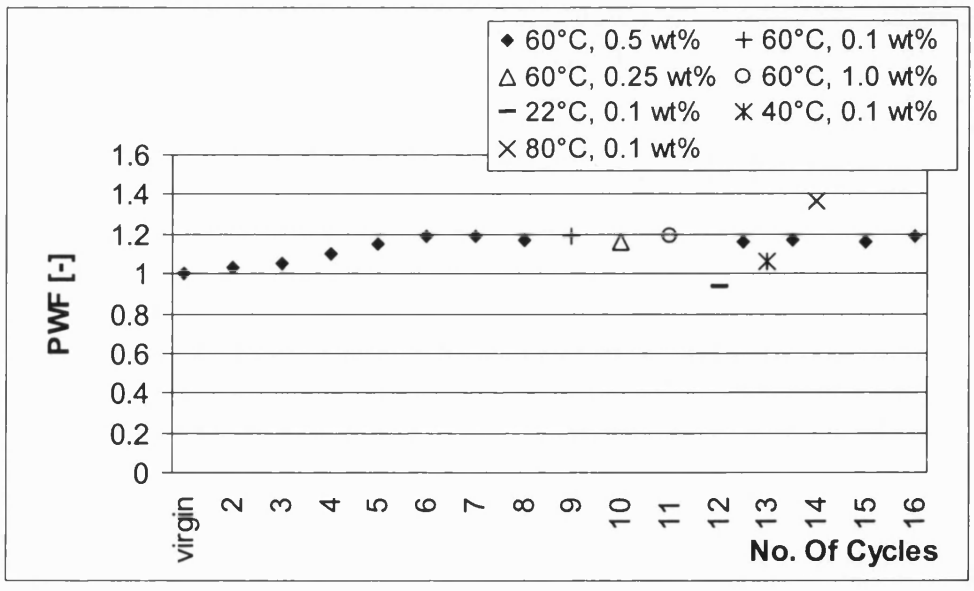


Figure 5.8(b): Pure water flux development after Ultrasil 11 cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.05wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% Ultrasil 11, 60°C, 1.9 ms^{-1}).

In Figure 5.8(a) the pure water fluxes are depicted, which were found after sodium hydroxide cleaning. The results confirm the product flux results. The PWF's keep on declining after a steady-state is reached at cycle 10.

In Figure 5.8(b) the pure water fluxes are depicted, that were found after *Ultrasil 11* cleaning. It shows clearly the influence of adsorption of surfactants, in particular nonionics. The hot wash (60°C) appears to lead to a very high adsorption of non-ionics. In comparison to the cold wash, where an initial decline could be seen, the effect of surfactant adsorption using a hot wash is very impressive. And in comparison to sodium hydroxide cleaning the performance after *Ultrasil 11* is impressively different, even raising the flux above the value of that of the pristine membrane. It is interesting to see that over the first six cycles the pure water flux increases continuously to reach a steady state ca. 20% above the original value of the virgin membrane. Due to the accumulation of fouling material the membrane surface becomes more hydrophobic, which is proven by the contact angle measurements (see results contact-angle in part I; section 4.1). This will enhance the adsorption of surfactants and hence turn the surface to a more hydrophilic value.

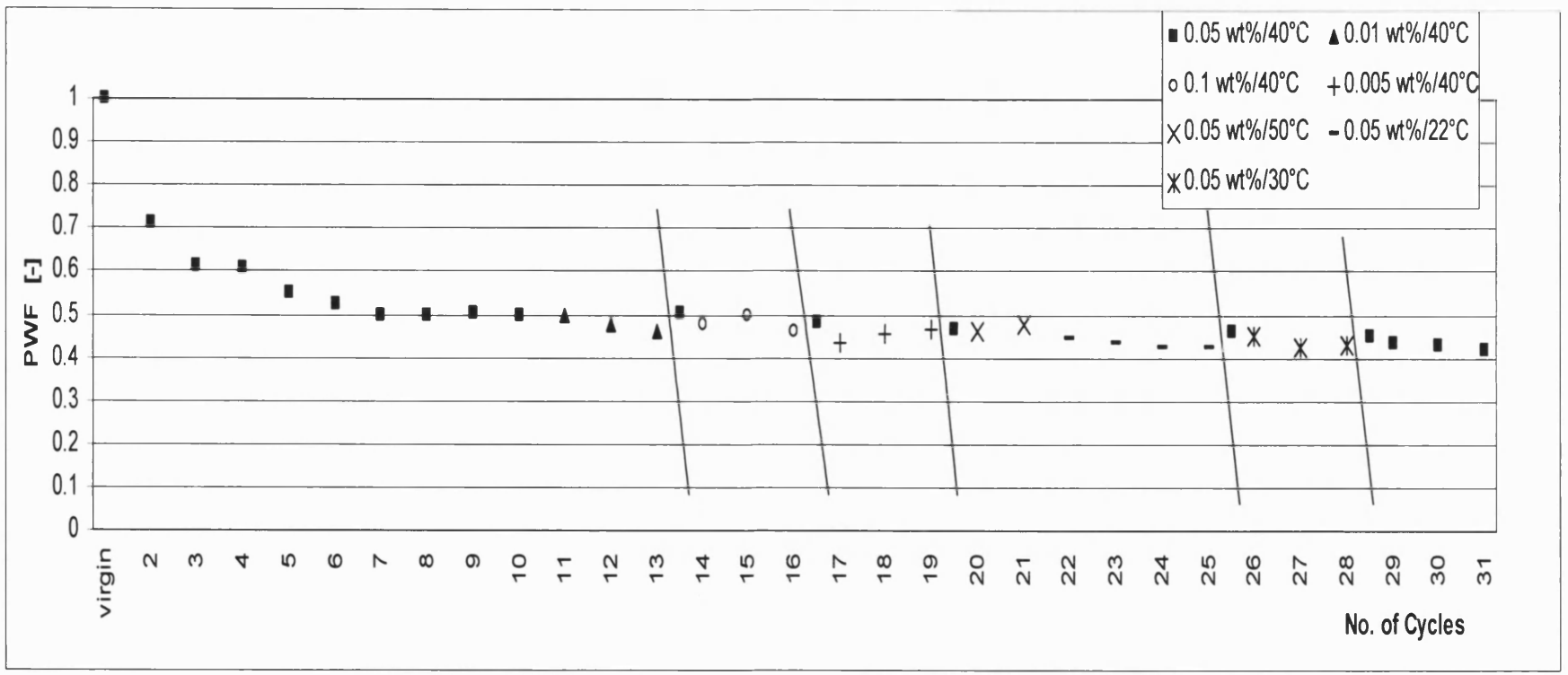


Figure 5.9(a): Pure water flux development after NaOH cleaning of VHV-S fouled regenerated cellulose membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% NaOH, 40°C, 1.9 ms^{-1}).

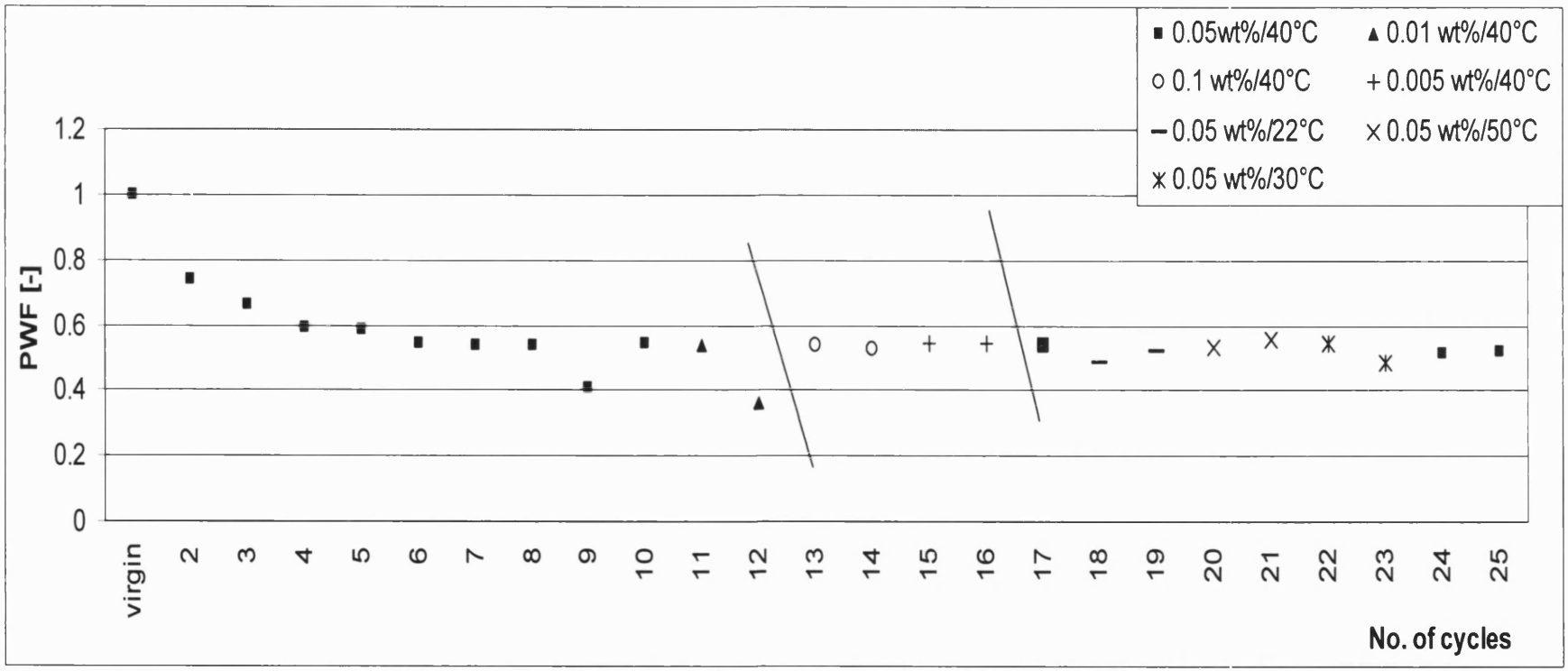


Figure *5.9(b): Pure water flux development after Ultrasil 11 cleaning of VHV-S fouled regenerated cellulose membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}).*

In Figure 5.9(a) the pure water fluxes found after sodium hydroxide cleaning of regenerated cellulose membrane are depicted. The PWF drops about 50% and enters then a steady state, when the membrane is cleaned with sodium hydroxide. This decline confirms the results for the product flux. According to the flux decline, there is a considerable amount of fouling occurring, but not as severe as that seen for the PES membrane. It seems that the very hydrophilic cellulose repels hydrophobic material to a certain degree, but not entirely. Other mechanisms which enhance fouling will also play their part, like surface roughness and pore size distribution. These parameters were not determined for the RC membrane.

In general, the composition of the fouling material adsorbed on the membrane will shift from hydrophobic molecules towards more hydrophilic ones. This can be seen in the extraction results, where triglycerides and esters emerge in much greater amounts at the PSf than for the more hydrophobic PES membrane. As a result a cleaning agent when used for hydrophilic membranes is facing a different type of foulants. Thus, the cleaning mechanism for hydrophilic membranes differs from hydrophobic membranes. This difference is mainly based on tow factors. In wood based liquors, the majority of foulants are of hydrophobic nature. They will not adsorb on hydrophilic surfaces and therefore over the short term there will be less fouling in contrast to hydrophobic membranes. And secondly; the amphiphilic molecules will adsorb with their hydrophilic part towards the surface, hence making the surface after long term gradually more hydrophobic. In the case for *Ultrasil 11* cleaning this applies as well for example for the anionic surfactants.

For the PWF after *Ultrasil 11* cleaning of a regenerated cellulose membrane the same can be stated what was already said for the product flux. There is no significant attachment of nonionic surfactants, which could dramatically enhance the pure water flux as can be seen for PES membrane. What probably happens is that anionic surfactants attach with their heads towards the membrane surface. Along with some foulants, that will make the membrane slightly more hydrophobic, which could support the attachment of nonionics. Therefore, the PWF is not dropping as much as it can be seen when cleaning with sodium hydroxide. EDTA is of insignificant use, since adsorption due to hydrophobicity is not important. Overall, it is a matter of economical consideration if an expensive cleaning agent such as *Ultrasil 11* is used

for a hydrophilic membrane, where the minor components may have little effect until the membrane is fouled considerably.

5.2.2.3 Retention

In the following figures the total solid retention of PES and RC membrane after NaOH and *Ultrasil 11* cleaning can be seen.

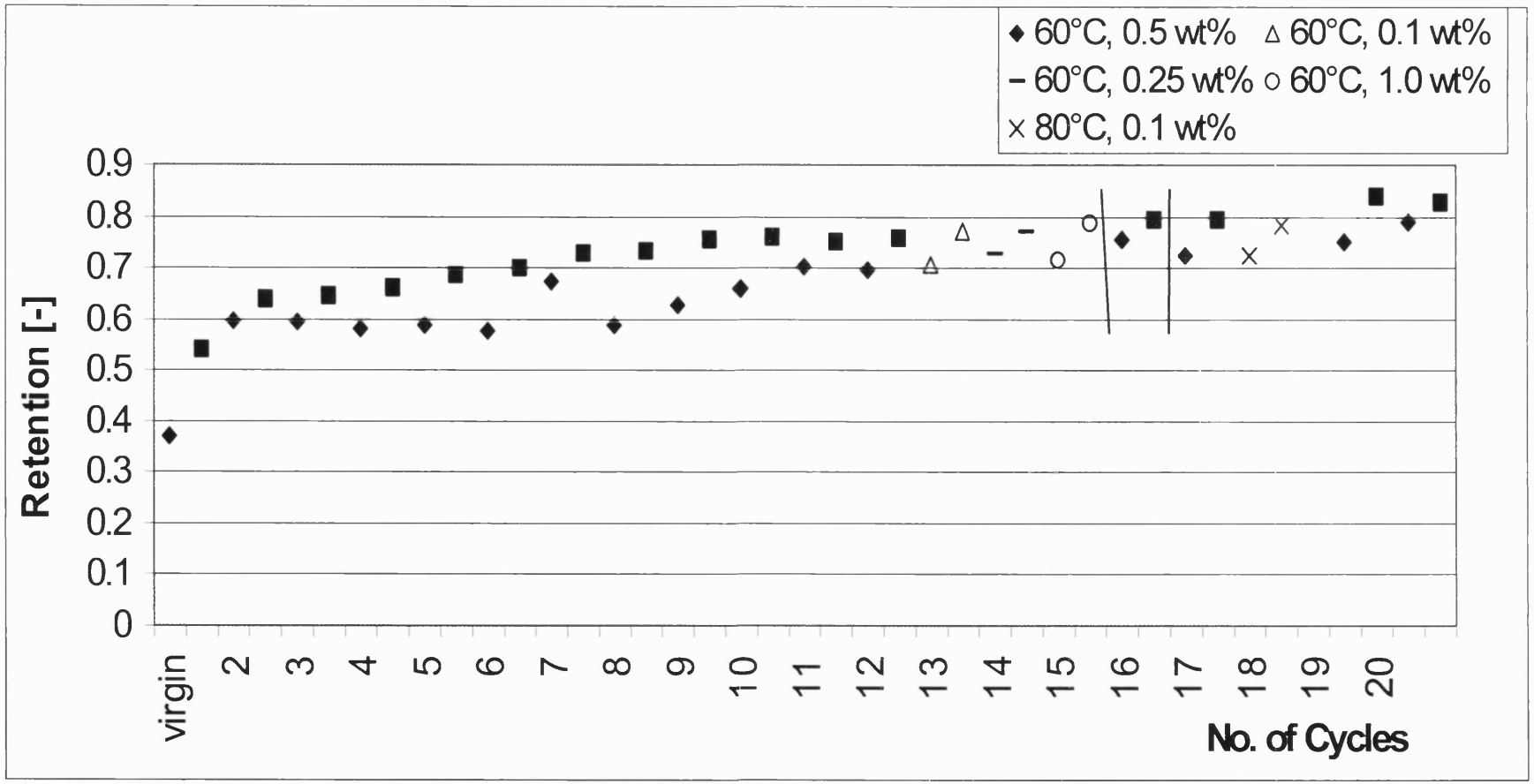


Figure 5.10(a): Retention of total solid content measured as TOC after NaOH cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.5wt% NaOH, 60°C, 1.9 ms^{-1}).

◆ *start value;* ■ *final value.*

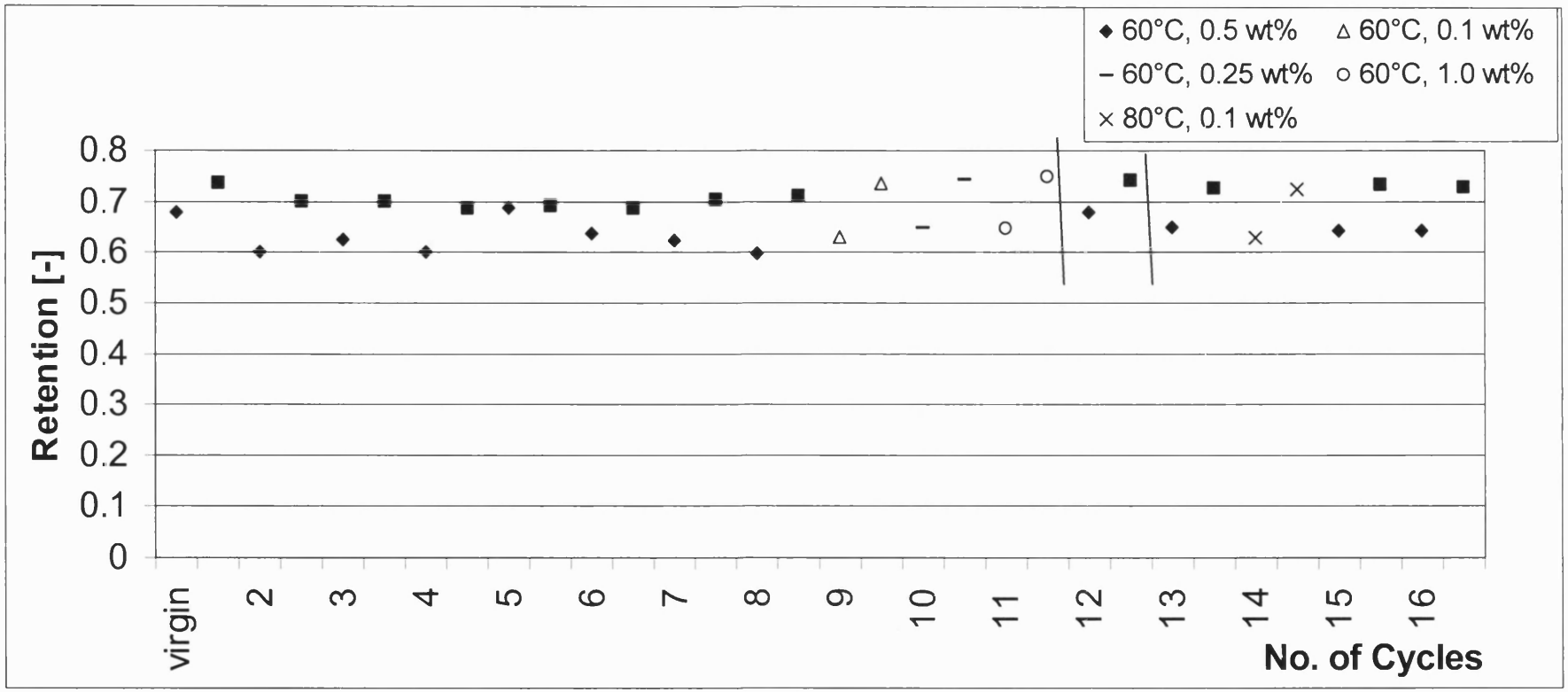


Figure 5.10(b): Retention of total solid content measured as TOC after Ultrasil 11 cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.5wt% Ultrasil 11, 60°C, 1.9 ms^{-1}). ◆ start value; ■ final value.

In Figure 5.10(a) the development of retention after sodium hydroxide cleaning of PES membrane is shown. Retention values reveal more about the fouling and cleaning mechanism than the product and pure water flux could do on its own. For example the product flux establishes a steady-state condition, where further decline is negligible small. But looking at the retention such a steady state is never established. In the beginning there is a sharp increase followed by a smaller but continuing increase. This clearly indicates that fouling material is building up and pores are getting narrower, hence increasing the retention. Ultimately the pores would get completely blocked when cleaned with sodium hydroxide. According to *Dal-Cin and co-workers* 1996 pore plugging is the most significant fouling mechanism when working with UF membranes and wood pulp. Why the pure water and the product flux have reached a quasi steady state, where the retention continues to increase at the same time is hard to answer. But the point is that retention is measured by the flow of spacious, bulky and charged molecules through the pores, whereas the pure water flux is solely dependent on the flow of very small water molecules. The product flux mainly depends upon the flux of water. That means, if a pore is narrowed that will have a small effect on the water flux, but a big effect on the flow of large molecules, *Lipnizki et al. 2002*. In order to understand it more clearly the reader should imagine a spherical molecule (which Lignosulphonates apparently is thought to be), which can **just** pass the pore. Then due to further fouling and cleaning, the pore is slightly narrowed. This has a devastating impact on the spherical molecule, since suddenly it cannot pass. Conversely, the small water molecules can still freely pass, and are only affected to a negligible degree. This can be seen precisely when looking at retention, with a considerable large increase over long term and pure water flux and product flux with a negligible small decline over long term.

In Figure 5.10(b) the retention is shown, after *Ultrasil 11* cleaning of the PES membrane. The retention is not increasing; hence the pores remain open. When cleaned with *Ultrasil 11* the hydrophobicity of the membrane surface changes to more hydrophilic values. This also affects the retention, grading to slightly higher values. It appears that a higher flow of water molecules pulls other molecules with it along through the pore, therefore the slight increase of retention.

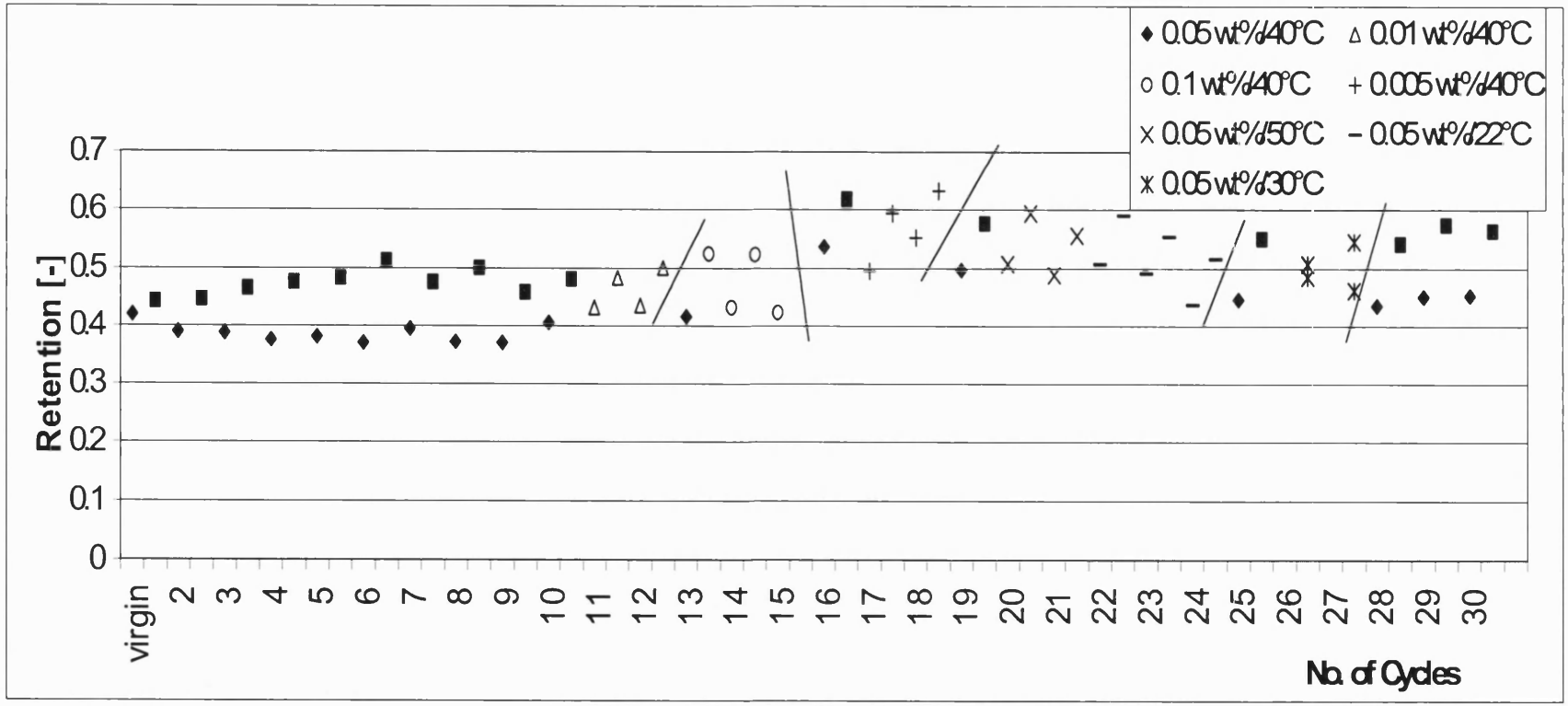


Figure 5.11(a): Retention of total solid content measured as TOC after NaOH cleaning of VHV-S fouled RC membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% NaOH, 40°C, 1.9 ms^{-1}).

◆ start value; ■ final value.

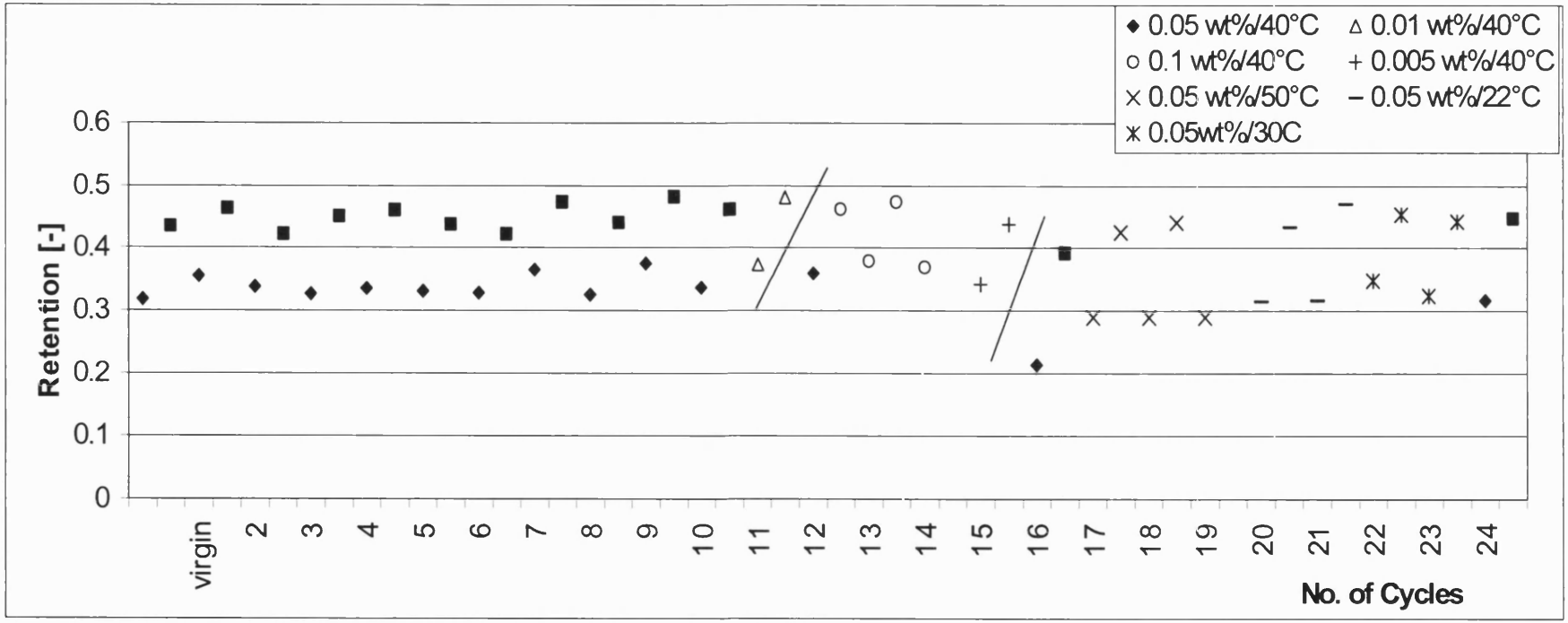


Figure 5.11(b): Retention of total solid content measured as TOC after Ultrasil 11 cleaning of VHV-S fouled RC membrane (protocol 2; Cleaning: 0.05wt%, 40°C, 1.9 ms^{-1}). Straight lines between the cycles denote additional wash carried out (0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}). ◆ start value; ■ final value.

In Figure 5.11(a) the retention of total solids content is shown (measured with TOC), which were found after sodium hydroxide cleaning of RC membrane. As can be seen the increase is much smaller than for PES membrane. This indicates that fouling and pore narrowing is much smaller than for PES. Pore blocking does not seem to be a dominant mechanism for filtration with RC membranes.

In Figure 5.11(b) the retention is shown, after *Ultrasil 11* cleaning of the RC membrane. There is virtually no decline and over long term even a slight increase can be seen. This increase can be explained by the gradual accumulation of non-ionic surfactants on the surface hence making it more hydrophilic and repelling.

5.2.2.4 Cleaning effect on rinsing

In the following pictures the effect of NaOH and *Ultrasil 11* cleaning of PES and RC membranes on rinsing behaviour is shown.

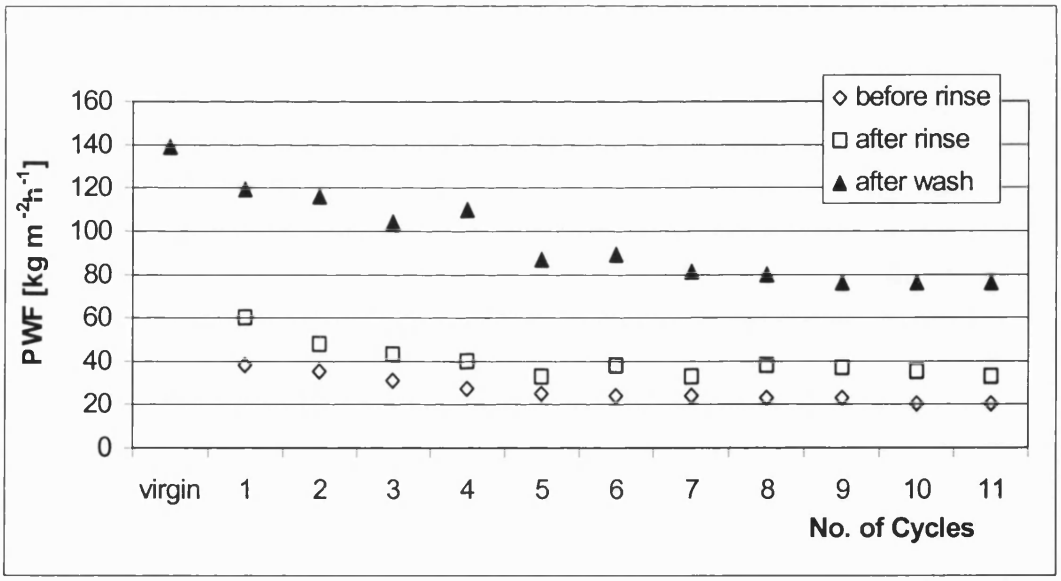


Figure 5.12(a): Pure water flux development before and after rinsing with pure water and after NaOH cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}).

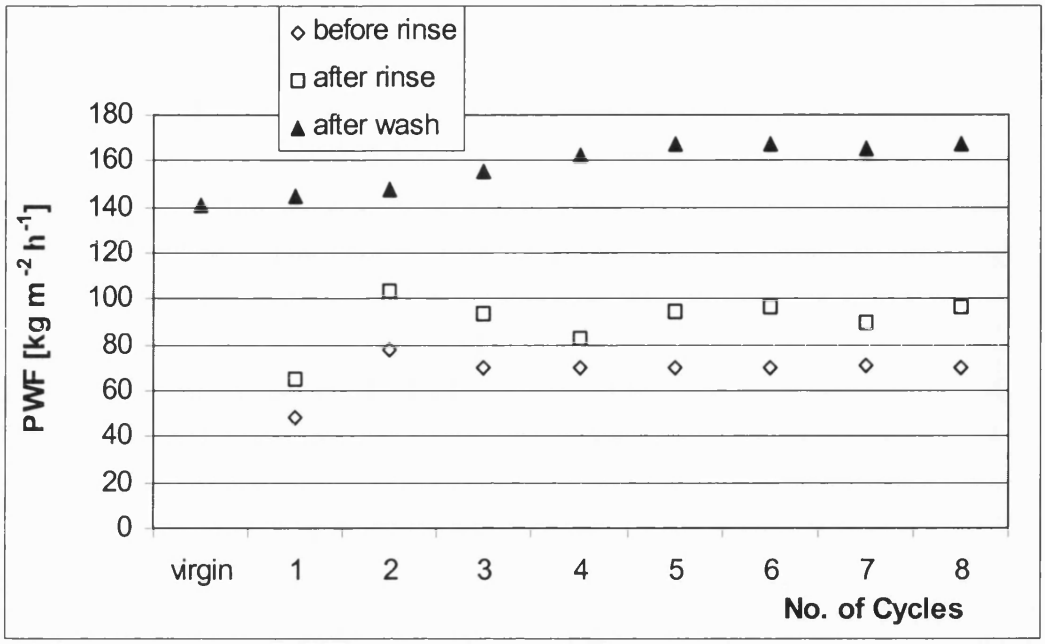


Figure 5.12(b): Pure water flux development before and after rinsing with pure water and after Ultrasil 11 cleaning of VHV-S fouled PES membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}).

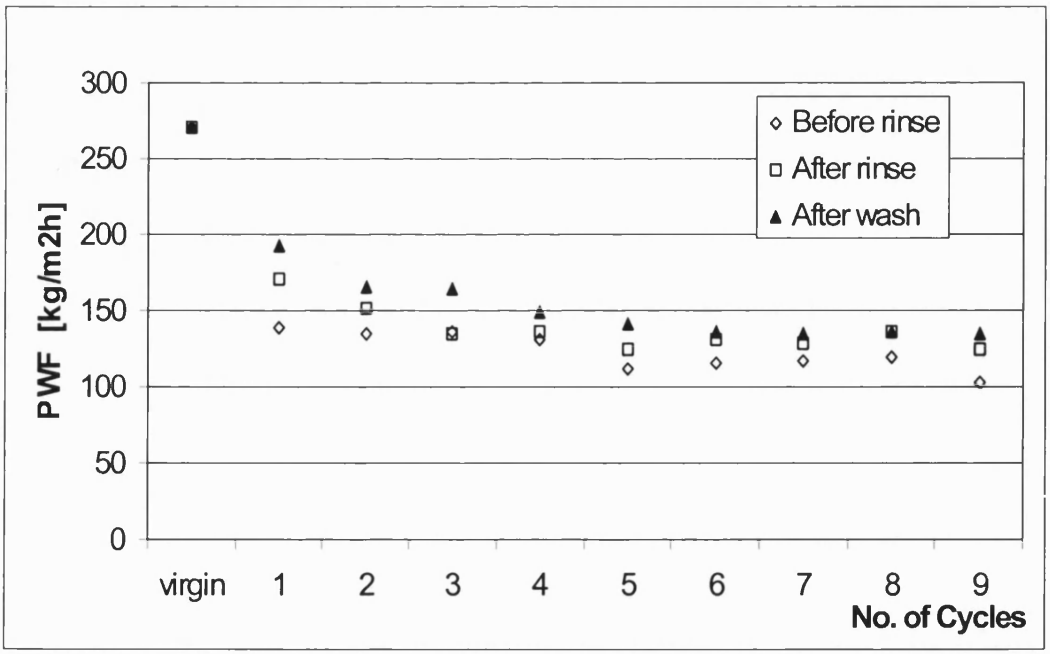


Figure 5.13(a): Pure water flux development before and after rinsing with pure water and after NaOH cleaning of VHV-S fouled RC membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}).

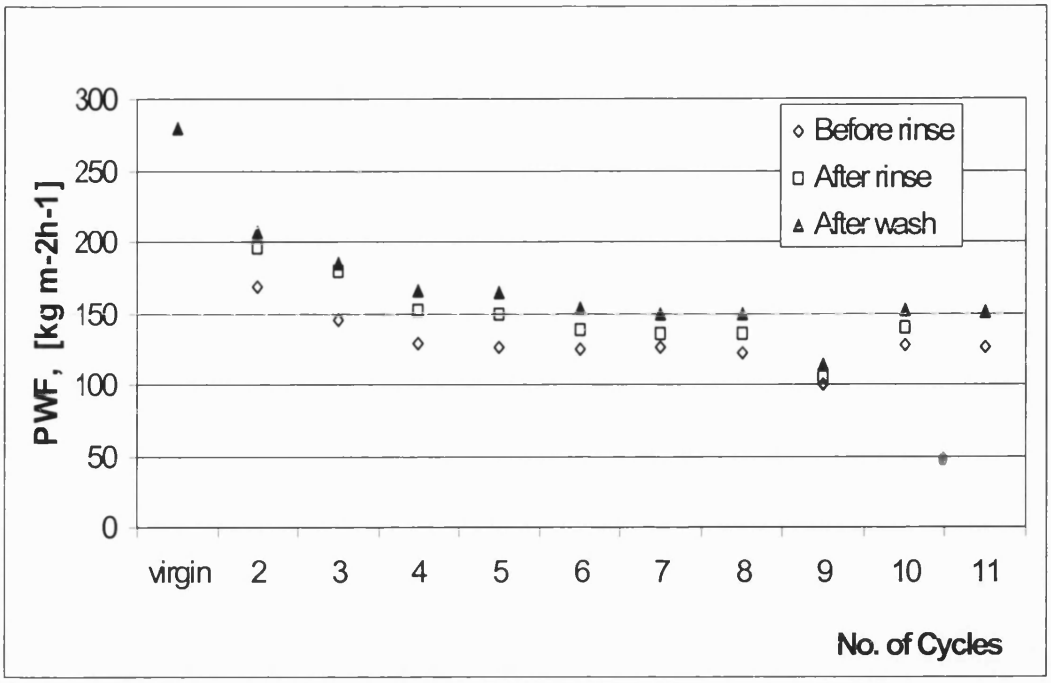


Figure 5.13(b): Pure water flux development before and after rinsing with pure water and after Ultrasil 11 cleaning of VHV-S fouled RC membrane (protocol 2; Cleaning: 0.5wt%, 60°C, 1.9 ms^{-1}).

Figure 5.12(a) shows the pure water flux before and after rinsing with pure water and after cleaning with sodium hydroxide for a PES membrane fouled with VHV-S. The values are displayed in kg $m^{-2}h^{-1}$. The result of rinsing is also important to display. When just the pure water flux development after cleaning is shown, the trend for cleaning over many cycles can be followed. It will not tell us anything about the efficiency of the cleaning step itself within one cycle. This information can be retrieved when all pure water flux values are displayed. Cleaning of PES membrane with sodium hydroxide is approximately 1/3 more effective in the initial stages up to cycle 7 in contrast to when the steady state is reached. The effect of rinsing remains the same over the whole number of cycles carried out. The drop in performance between the virgin membrane and cycle 7 for PWF **before rinsing** is about 15 kg $m^{-2}h^{-1}$. The drop of performance between virgin membrane and cycle 7 for PWF **after rinsing** is about 20 kg $m^{-2}h^{-1}$. The drop in performance between virgin membrane and cycle 7 for PWF **after washing** is about 60 kg $m^{-2}h^{-1}$ For the rinsing process itself, sodium hydroxide cleaning seems to reduce the effect of rinsing. The amount

reduces from 20 kg $m^{-2}h^{-1}$ for the 1st cycle (virgin membrane) to 10 kg $m^{-2}h^{-1}$ for all the rest of the cycles. When cleaning with a chemical cleaning agent is carried out, the gel layer is largely removed, which allows big changes in PWF recovery. Close range to the membrane surface, adsorption of foulants takes place, which in dependency upon the cleaning agent and the membrane material, the surface hydrophobicity and charge (see contact angle and zeta-potential results; section 4.2 and 4.4).

As already explained for Figure 5.1(a), the cleaning efficiency will decrease until equilibrium on the surface is established when the drive of the hydrophilic head group toward the water equals the drive of the hydrophobic moiety of foulants towards the surface. This is mirrored by the PWF results after cleaning.

Figure 5.12(b) shows the pure water flux before and after rinsing with pure water and after cleaning with *Ultrasil 11* on the PES membrane. An increasing cleaning performance can be seen, which confirms previous results from the product flux. In contrast to Figure 5.12(a), cleaning with NaOH, a big change in performance can be seen for the values before and after rinsing for the 2nd cycle. Nonionic surfactants start to get attached to the membrane surface and raise the hydrophilicity. This firstly increases the pure water flux before rinsing even though the gel layer has not yet been removed. Secondly, the increased hydrophilicity helps to remove the gel layer during rinsing.

Figure 5.13(a) shows the pure water flux before and after rinsing with pure water and after cleaning with sodium hydroxide for RC membrane. Similar to the PES membrane graphs the cleaning shows a declining trend whereas the rinsing is already at a steady-state after the 2nd cycle. Looking at this graph it becomes clear that sodium hydroxide does show a cleaning effect, at least at the beginning. After cycle 4 though, sodium hydroxide does not show any additional effect for rinsing. It is interesting to see that the membrane material is lowering the scale of the gel layer. As explained earlier, adsorption of more amphiphilic foulants take place. Therefore, sodium hydroxide does not play such a big role in interacting with the foulants, because foulants are more hydrophilic and secondly there are not so many foulants to

react with. Thus equilibrium is established earlier in comparison to the PES membrane.

Figure 5.13(b) shows the pure water flux before and after rinsing with pure water and after cleaning with *Ultrasil 11* on RC membrane. The cleaning is very poor when using *Ultrasil 11* on RC membranes. Here it becomes much clearer that hardly any removal of foulants takes places. The attachment of non-ionic surfactants on the long run seems to support the removal of the gel layer when rinsed.

5.3 Impact of Concentration and Temperature

In the graphs for product, pure water flux and retention the effect of concentration and temperature change of cleaning solutions is displayed after the steady-state was reached. Determination of the concentration and temperature optima was carried out in the early stages of the project for only once-fouled membrane. This is the scientific approach numerous researchers have been using in the past to test membranes upon their foulability and cleanability and to draw conclusions. However, results obtained from this approach are rather useless for industrial applications. As already shown, the performance will change over time depending on the cleaning agent and membrane used. A good performance over the short term (or long the term) can be inverted over long term (or short term). In addition, industry is simply more interested in the cleaning behaviour of heavily fouled membranes rather than freshly fouled membrane. Therefore, it would be more beneficial if long term fouled membranes could be tested upon their cleanability when process parameters are changed. Unfortunately, no reference value exists to determine the effect of cleaning for long term fouled membranes. For once-fouled membranes the flux of the pristine, virgin membrane can be used as a reference, but for long term fouled membranes, there is no consistent value which could be used as a measure of cleanliness. However, it was assumed that the steady-state cleaned membrane flux value could be used for this purpose. Even though this quasi steady-state shows a small declining trend over many cycles, it is good enough as a reference, because

such a small long term decline can be taken into account. If the performance drops due to insufficient cleaning significantly below this steady-state value, an additional wash could be carried out to restore the value. In this sense experiments were carried out over the long term, and the results can be seen in the graphs already presented. The results are presented for the sake of completeness, in order to enable the reader to see the whole set of results, in connection with the initial stages of decline. Taken from there the results are picked out and presented as Histograms, which makes interpretation somewhat easier.

Firstly, the results for one fouling and cleaning cycle are presented:

5.3.1 Impact of concentration and temperature changes after short term fouling (one time).

In the following histograms, the result of concentration and temperature changes of NaOH and *Ultrasil 11* cleaning solution is diagrammed on product and pure water flux of short term fouled (one cycle) PES and PSf membranes.

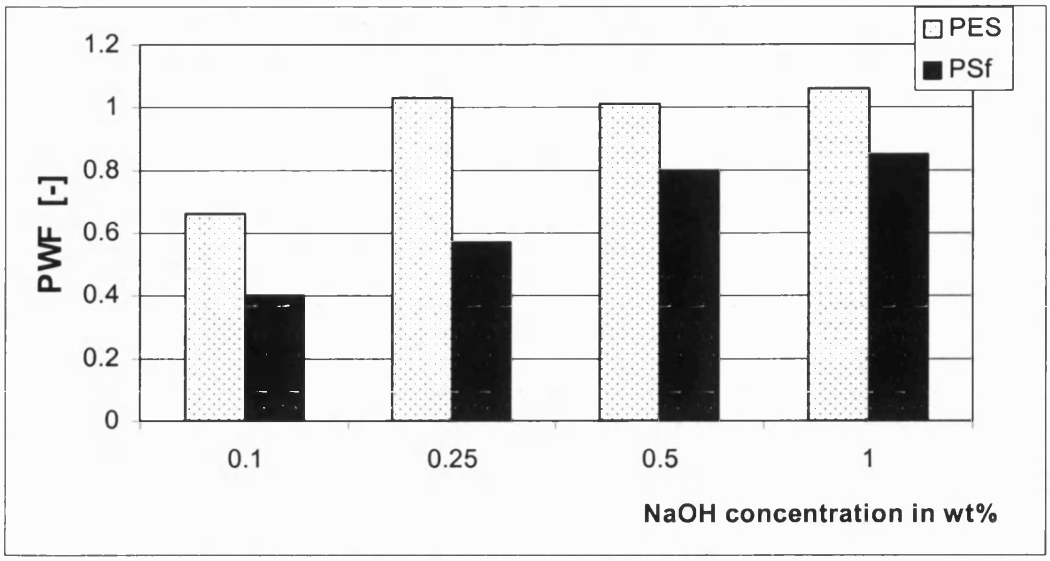


Figure 5.14(a): PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane with different concentrations of NaOH (Protocol 1; 22°C, 1.9 ms^{-1}).

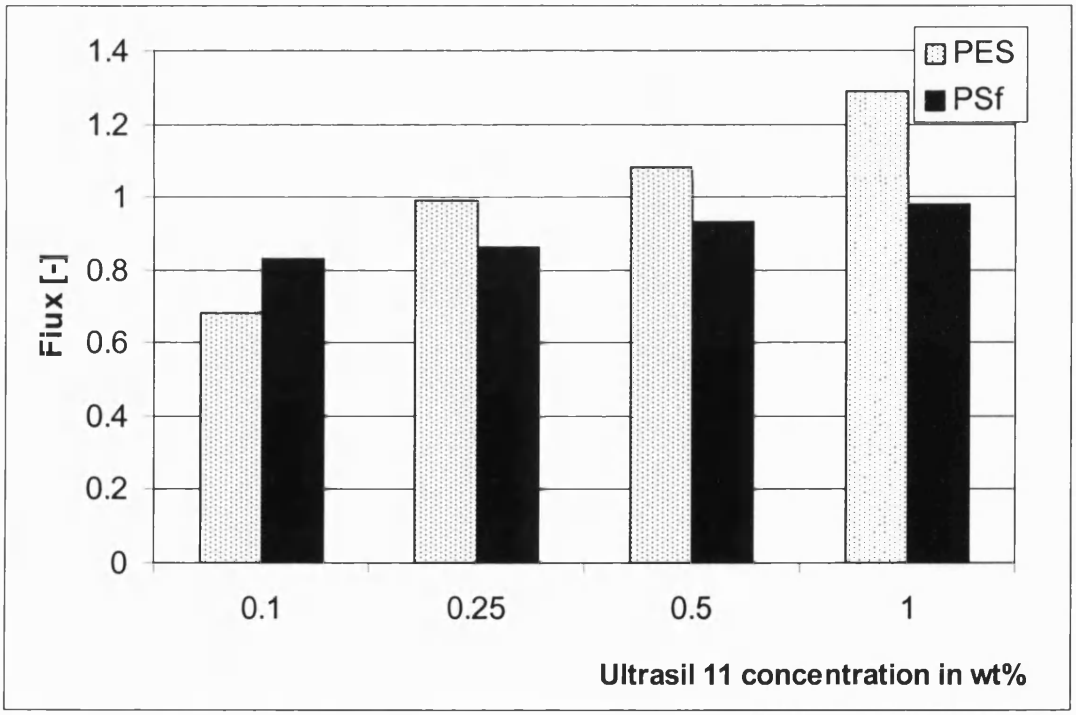


Figure 5.14(b): PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane with different concentrations of Ultrasil 11 (Protocol 1; 22°C, 1.9 ms^{-1}).

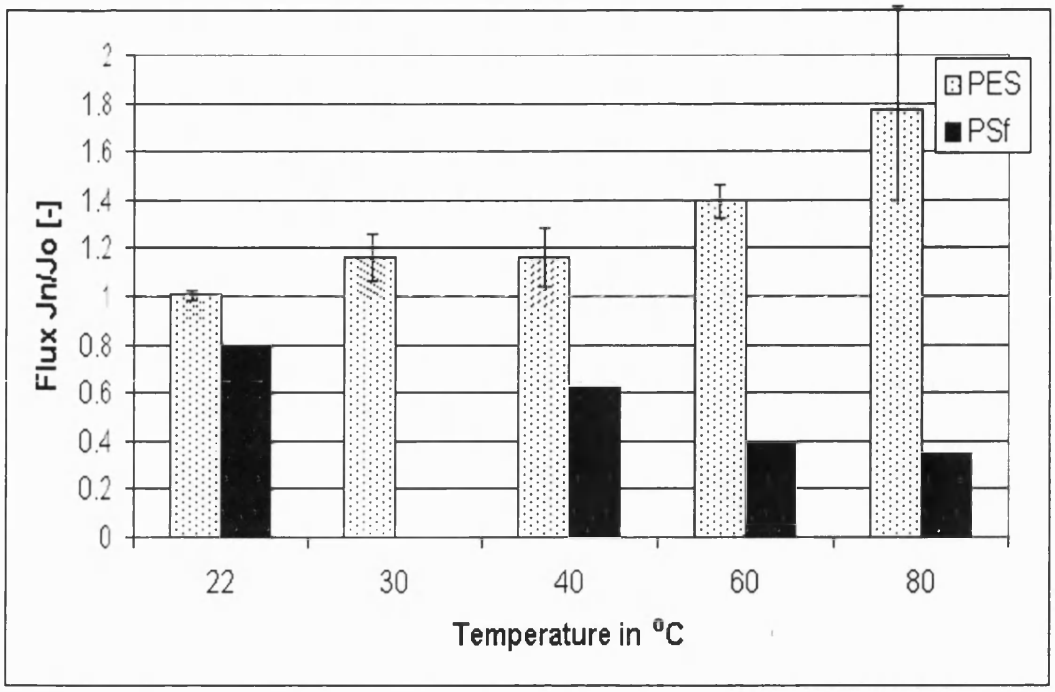


Figure 5.15(a): PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane with different NaOH solution temperatures (Protocol 1; 0.5wt% NaOH, 1.9 ms^{-1}).

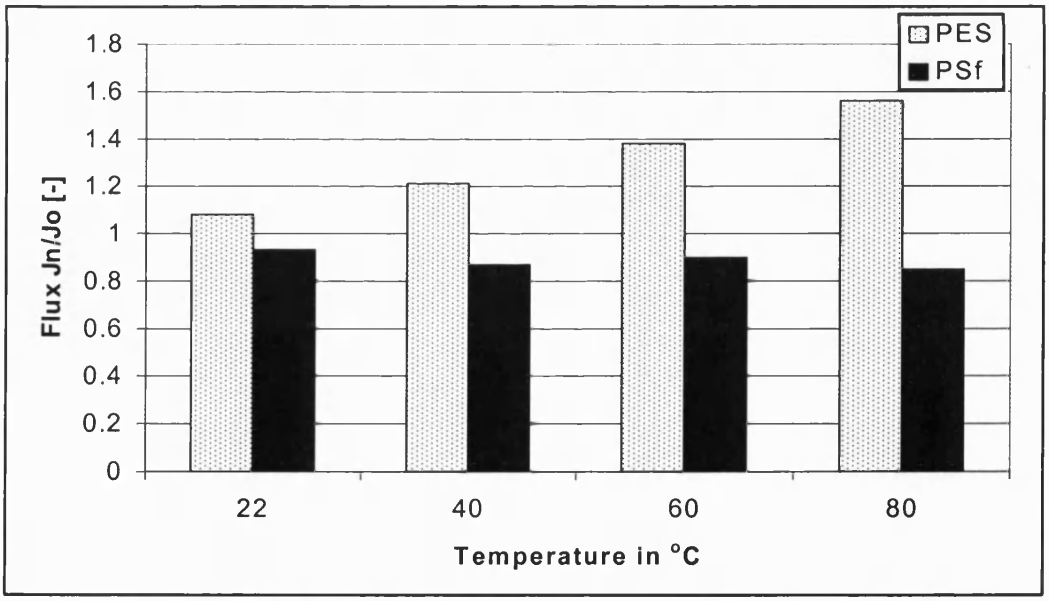


Figure 5.15(b): PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane with different Ultrasil 11 solution temperatures (Protocol 1; 0.5wt% Ultrasil 11, 1.9 ms^{-1}).

In Figure 5.14(a) the PWF recovery after cleaning of single fouled PES and PSf membrane with different concentrations of NaOH solution can be seen. PES membrane shows only at the lowest concentration of 0.1wt% a drop of performance below that of the virgin membrane. For the PSf membrane there is a clear performance improvement with increasing concentrations. PSf has a much lower pore size distribution than PES. Pore blocking is therefore more severe than for PES, hence increases in concentration have a greater effect on PWF recovery.

In Figure 5.14(b) the PWF recovery after cleaning of single fouled PES and PSf membrane with different concentrations of *Ultrasil 11* solution can be seen. This time for PES membrane a clear increase can be seen due to the increase of *Ultrasil 11* concentration. The recovery values are in general low because of cleaning at 22°C. At such "cold" temperatures the adsorption of nonionic surfactants is low even for hydrophobic materials and even lower for more hydrophilic materials. PSf is more hydrophilic than PES, hence the smaller increase in comparison with PES. If Figures 5.14(a) and 5.14(b) are compared, the effect of surfactant adsorption becomes clearly visible. For PES at a concentration of 0.1wt% no surfactant adsorption can be seen and the performance is the same, whether the membrane is NaOH or *Ultrasil 11* cleaned. At higher concentrations the PWF recovery of the PES membrane when cleaned with NaOH stops at the value for the virgin membrane. *Ultrasil 11* clearly raises the PWF above the value of the pristine membrane. For PSf membrane the smaller pore size distribution has some impact on the cleaning at different concentrations. At low concentrations, the adsorption of surfactants on the PSf material is supporting the impact of NaOH on its own. At higher concentrations this adsorption of surfactants becomes less pronounced and the performance of *Ultrasil 11* compared with NaOH is almost the same. In total the surfactant adsorption on PES and its effect on PWF recovery is much bigger than for PSf. Particular nonionic surfactants adsorb preferably on hydrophobic surfaces. Therefore, the result makes a lot of sense, since PES is more hydrophobic, (Table 4.1 and 4.2) and has a higher surface area in comparison to PSf.

In Figure 5.15(a) the PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane at different NaOH solution temperatures is presented. For the PES membrane, each experiment was carried out four times in order to calculate the

standard deviations. As one can see, the performance improves when temperature is raised. This is clearly due to the complete removal of glycerine, since protocol 1 was used to condition the membrane. The increasing standard deviation supports this suggestion. Why the once fouled PSf membrane shows an even lower flux after cleaning at increasing NaOH solution temperatures is difficult to explain. A possibility could be that increased temperatures help sodium ions to react with lignosulphonates and the fouling layer becomes more compact.

In Figure 5.15(b) the PWF recovery after cleaning of single VHV-S fouled PES and PSf membrane with different *Ultrasil 11* solution temperatures can be seen. The good recovery for PES membranes cleaned with *Ultrasil 11* at elevated temperatures is probably due to both glycerine removal and surfactant adsorption. For the PSf membrane and *Ultrasil 11* cleaning a difference in PWF cannot be seen, which is probably due to surfactant adsorption at higher temperature, making the surface more hydrophilic hence enhancing the pure water flux.

5.3.2 Impact of concentration and temperature changes after long term fouling

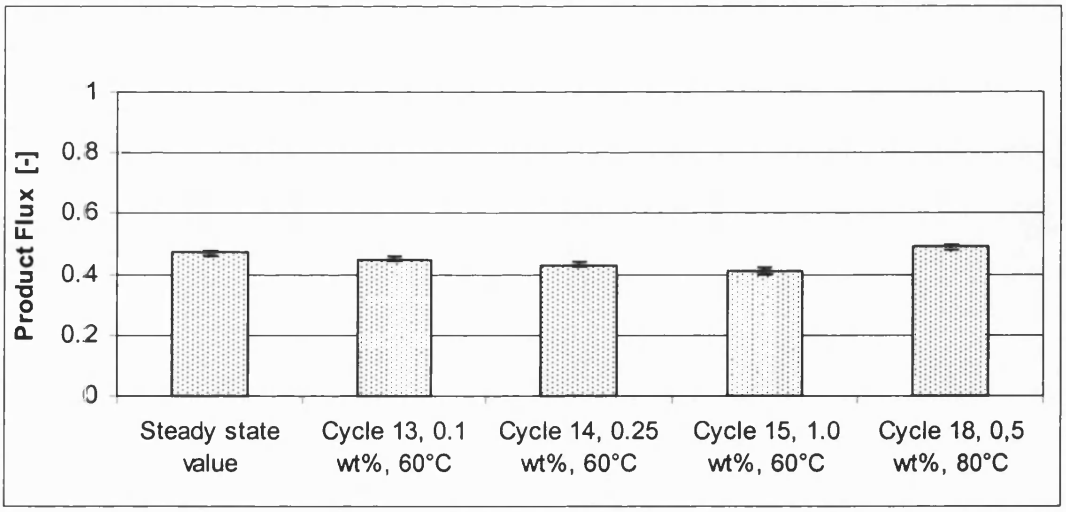


Figure 5.16(a): Product flux recovery after cleaning of multiple VHV-S fouled PES membrane with different NaOH solution concentrations and temperatures (Protocol 2; stead state = average from cycles 10-12;conditions 0.5wt% NaOH, 60°C, 1.9 ms^{-1}).

In the following histograms, the result of concentration and temperature changes of NaOH and *Ultrasil 11* cleaning solution is diagrammed on product and pure water flux of long term fouled PES and RC membranes.

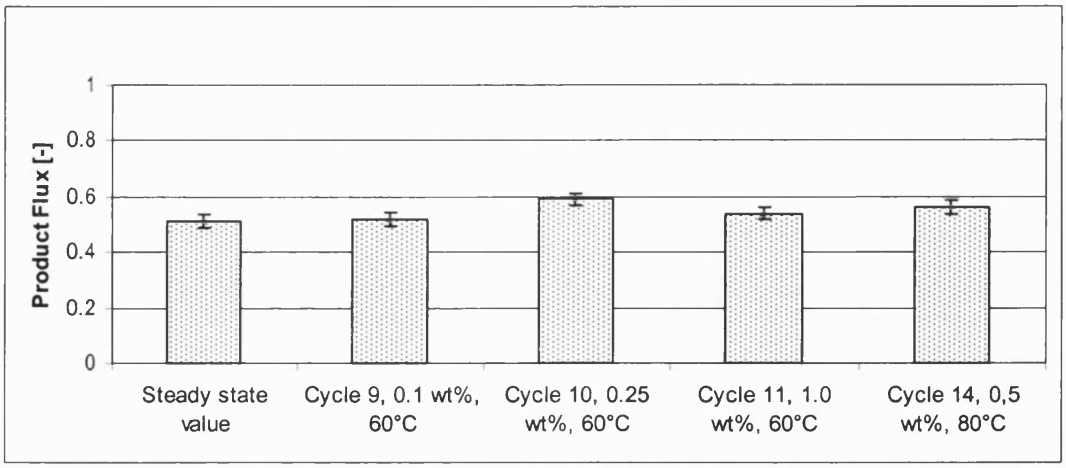


Figure 5.16(b): Product flux recovery after cleaning of multiple VHV-S fouled PES membrane with different Ultrasil 11 solution concentrations and temperatures (Protocol 2; steady state = average from cycles 6-8; conditions 0.5wt% Ultrasil 11, 60°C, 1.9 ms^{-1}).

In Figure 5.16(a) the product flux recovery can be seen after cleaning of multiple fouled PES membrane with different NaOH solution concentrations and temperatures. The change of NaOH concentration has no impact on flux recovery and cannot even prevent the natural decline occurring over each single cycle. In contrast temperature has a big impact as can be seen for cleaning at 80°C. The value is recovered even above the steady state value. Other temperatures are not displayed, because the pure water flux (note: not product flux) dropped down after cleaning at "colder" temperatures, hence making an additional cleaning necessary.

In Figure 5.16(b) the product flux recovery can be seen after cleaning of multiple fouled PES membrane with different *Ultrasil 11* solution concentrations and temperatures. Once again, changes of concentration seem to have no impact. As it will be shown later, this is convincingly proved by the pure water fluxes. In contrast to cleaning with NaOH, increasing the temperature shows no impact on the product flux. This is surprising, because it is shown later for the pure water fluxes, that cleaning at elevated temperatures indeed has a huge impact. It does not show up in the product fluxes, because further adsorption of surfactants stimulates the pure

water flux but to a lesser extent the product flux. And secondly, the other components in *Ultrasil 11*, such as EDTA and NaOH would have a better activity at high cleaning temperatures, but as it will be shown later, this has an impact in product fluxes only at subsequent cycles. It takes some time for the product flux to show the full effects of cleaning. Therefore, several cycles should be carried out in order to see the full impact of changed process parameters.

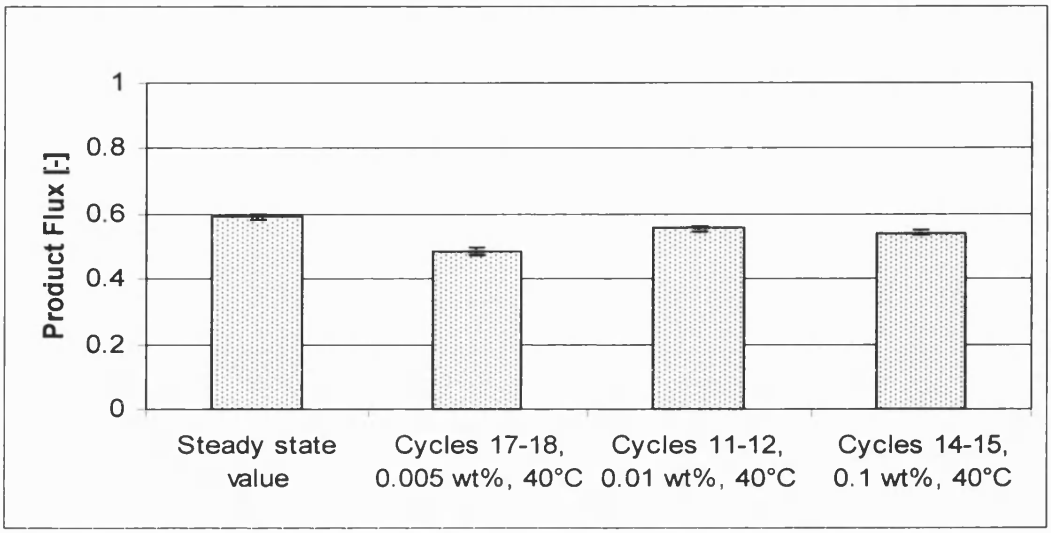


Figure 5.17(a): Product flux recovery after cleaning of multiple VHV-S fouled RC membrane with different NaOH solution concentrations (Protocol 2; steady state = average from cycles 8-10; conditions 0.05wt% NaOH 11, 40°C, 1.9 ms^{-1}).

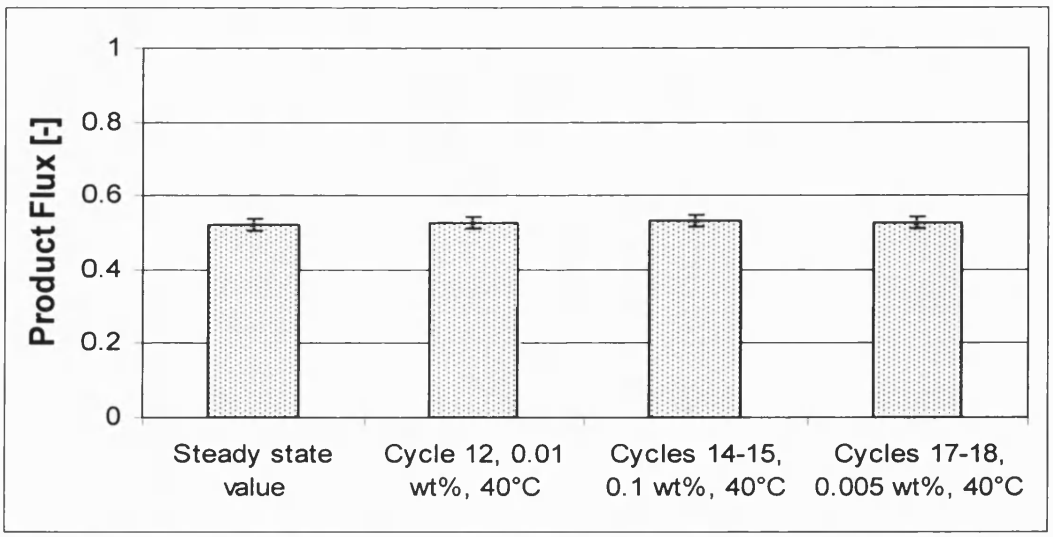


Figure 5.17(b): Product flux recovery after cleaning of multiple VHV-S fouled RC membrane with different Ultrasil 11 solution concentrations (Protocol 2; steady state = average from cycles 9-11;conditions 0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}).

In Figure 5.17(a) the product flux recovery after cleaning of multiple fouled RC membrane with different NaOH solution concentrations is displayed. For treatment of RC membrane 10 times smaller concentrations were used, because cellulose cannot withstand strong alkaline or acidic conditions. It becomes obvious that concentration does not have any impact on cleanability for the range tested experimentally. The obvious differences are due to the higher number of cycles and not due to any effect of cleaner. Only for a concentration of 0.005wt% a significant drop of performance can be seen. This is an extremely low solution concentration close to pure water.

For the variation of *Ultrasil 11* concentration in Figure 5.17(b) the change in performance is even smaller. In fact the performance remains very constant, even when the membrane is cleaned with 0.005wt%. It should be borne in mind that these histograms should be studied together with the graphs earlier presented for product flux. Each column in the histograms is calculated by averaging the results when more than 1 cycle was carried out for one concentration or temperature. Therefore, the slope of the subsequent flux decline or increase is also of importance and shows that each cycle is related to the subsequent one.

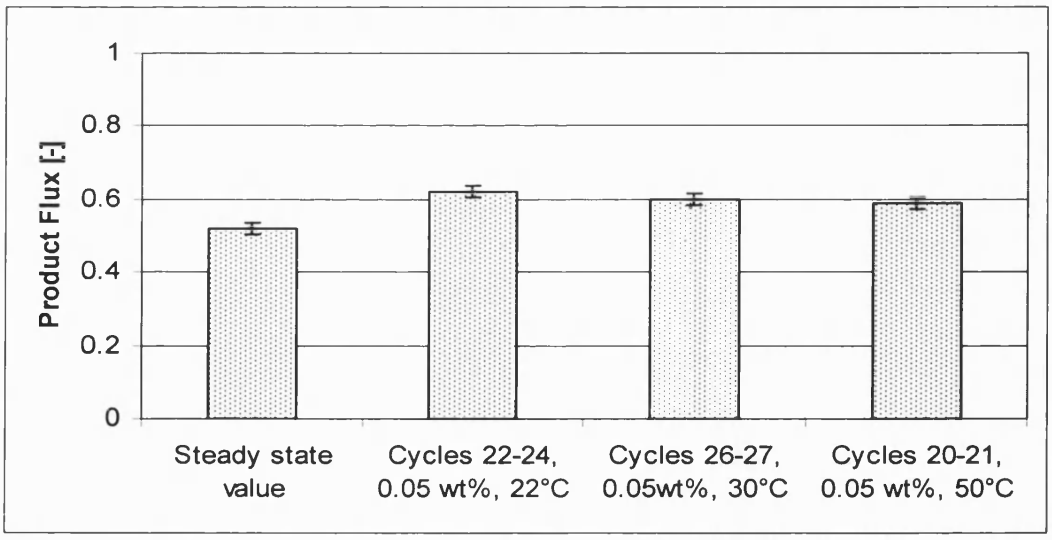
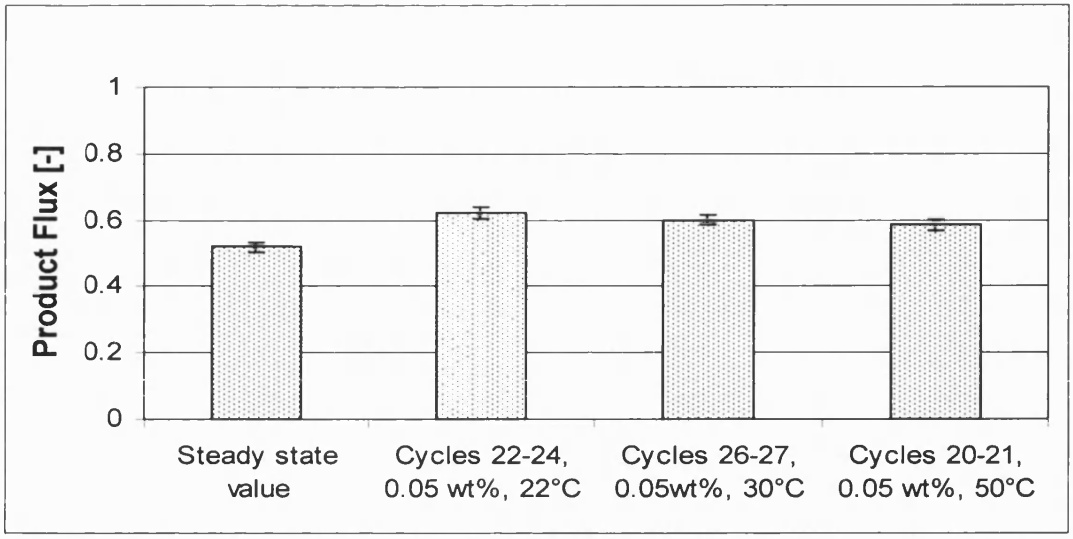


Figure 5.18(a): Product flux recovery after cleaning of multiple VHV-S fouled RC membrane at different NaOH solution temperatures (Protocol 2; steady state = average from cycles 8-10;conditions 0.05wt% NaOH, 40°C, 1.9 ms^{-1}).



5.18(b): Product flux recovery after cleaning of multiple VHV-S fouled RC membrane at different Ultrasil 11 solution temperatures (Protocol 2; steady state = average from cycles 9-11;conditions 0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}).

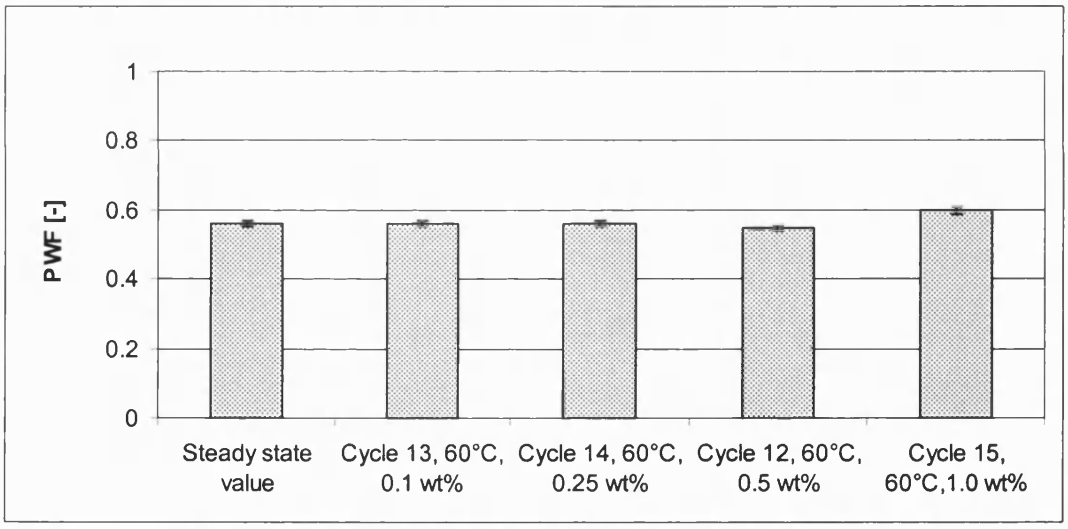


Figure 5.19(a): Pure water flux recovery after cleaning of multiple VHV-S fouled PES membrane with different NaOH solution concentrations (Protocol 2; steady state = average from cycles 8-10; conditions 0.5wt% NaOH 11, 60°C, 1.9 ms^{-1}).

In Figure 5.18(a) the product flux recovery after cleaning of multiple fouled RC membrane at different NaOH solution temperatures can be seen. Here, temperature

has a clear impact, but in total the change remains small, even when looking at the differences between cleaning at 22°C and at 50°C.

For *Ultrasil 11* cleaning of multiple fouled RC membrane (Figure 5.18(b)), a significant increase can be observed from the steady state value to the value obtained when cleaned at 50°C. Again, it should be borne in mind that these histograms should be studied together with the graphs earlier presented for product flux and the reader should not get confused with the fact that the flux is lower, when cleaned at higher temperature than it is for low cleaning temperatures. The set of experiments was started at a temperature of 50°C (Cycles 20-21). At this cycle number the membrane surface had already become more hydrophobic due to fouling and in addition high temperatures are favourable for surfactant adsorption. This has an overwhelming impact, so much so, that low temperature cleaning has no impact on reducing the performance when carried out in subsequent cycles, (Cycle 22-24 at 22°C and Cycles 26-27 at 30°C). As a result the pure water flux increases slowly over many cycles.

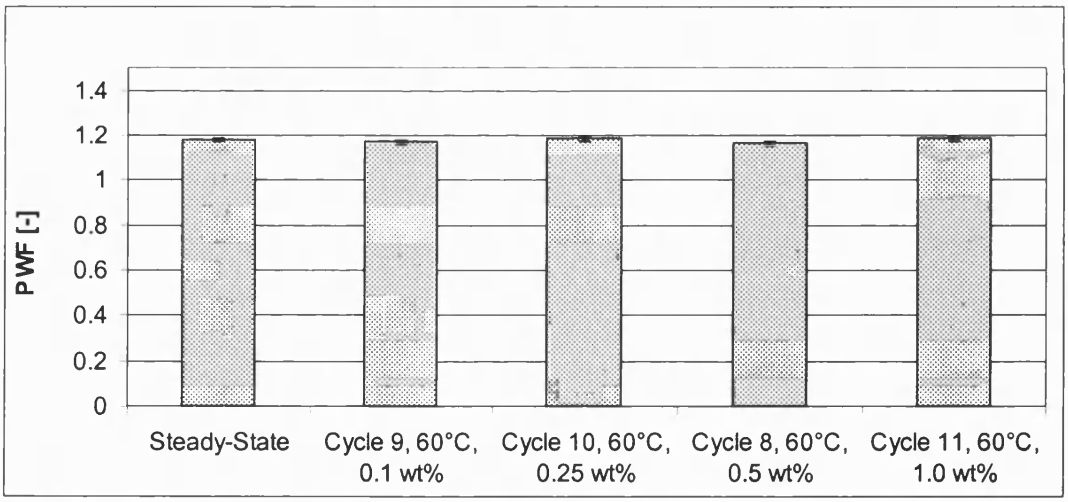


Figure 5.19(b): Pure water flux recovery after cleaning of multiple VHV-S fouled PES membrane at different Ultrasil 11 solution concentrations (Protocol 2; steady state = average from cycles 6-8; conditions 0.5wt% Ultrasil 11, 60°C, 1.9 ms^{-1}).

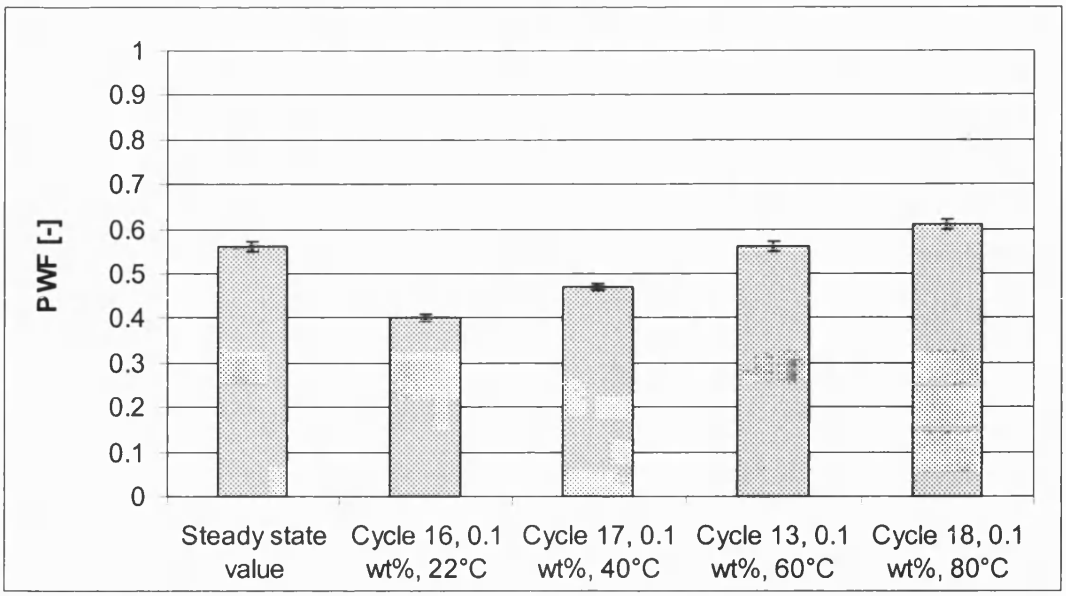


Figure 5.20(a): Pure water flux recovery after cleaning of multiple VHV-S fouled PES membrane at different NaOH solution temperature (Protocol 2; steady state = average from cycles 8-10; conditions 0.5wt% NaOH, 60°C, 1.9 ms^{-1}).

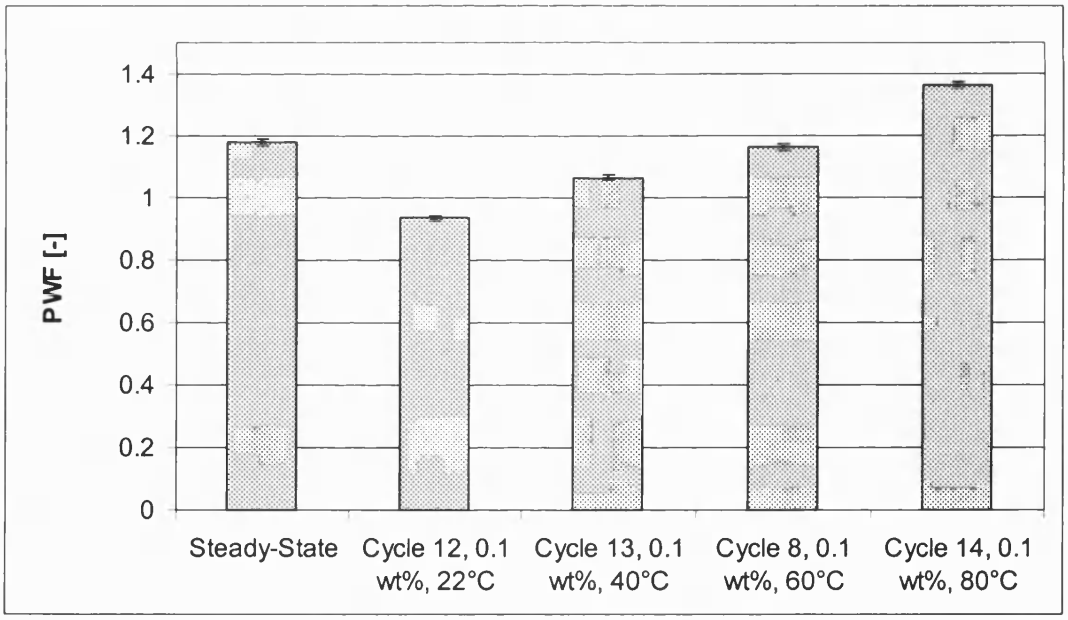


Figure 5.20(b): Pure water flux recovery after cleaning of multiple VHV-S fouled PES membrane at different Ultrasil 11 solution temperature (Protocol 2; steady state = average from cycles 6-8; conditions 0.5wt% Ultrasil 11, 60°C, 1.9 ms^{-1}).

In Figure 5.19(a) the pure water flux recovery is displayed after cleaning of multiple fouled PES membrane with different NaOH solution concentrations. As already seen for the product flux, the pure water flux does not show significant changes when the concentration of NaOH is altered within the range examined. Only when an excessive amount of NaOH is used (1.0 wt%) a small improvement can be seen. This improvement is unlikely to justify the use of such exorbitant amounts. For *Ultrasil 11* (Figure 5.19(b)) the same trend is seen, with no change when the concentration of Ultrasil 11 is altered.

When temperature is altered a very different picture is presented, (Figures 5.20(a) and 5.20(b)). Both agents show significant performance differences when temperature is altered, with a poor performance at "cold" cleaning and steadily increasing performance when the temperature is raised. The main difference between NaOH and *Ultrasil 11* cleaning is that for NaOH the PWF recovery remains below the value of the virgin membrane, whereas *Ultrasil 11* is raising it far above it.

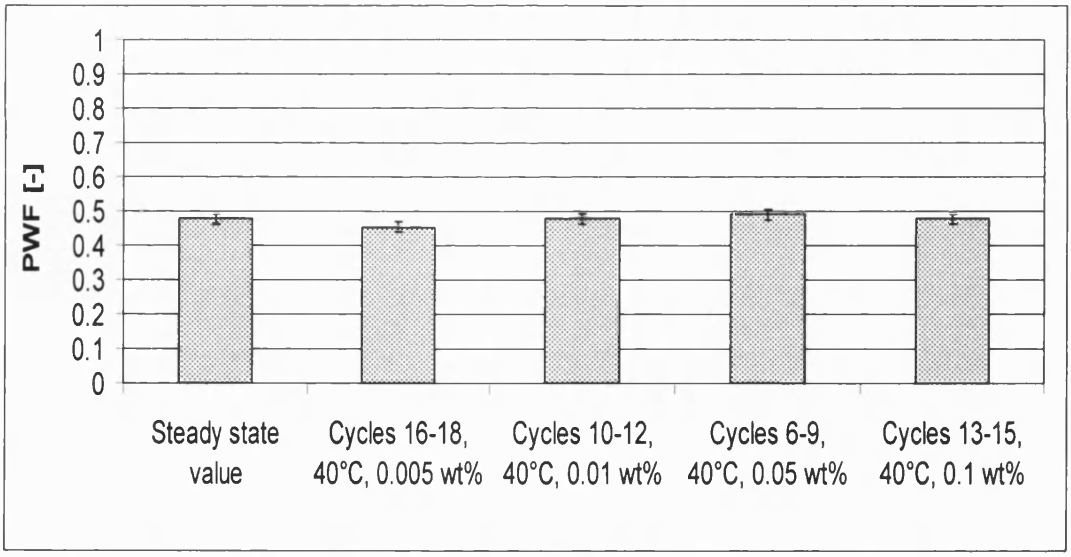


Figure 5.21(a): Pure water flux recovery after cleaning of multiple VHV-S fouled RC membrane at different NaOH solution concentrations (Protocol 2; steady state = average from cycles 6-9; conditions 0.05wt% NaOH, 40°C, 1.9 ms^{-1}).

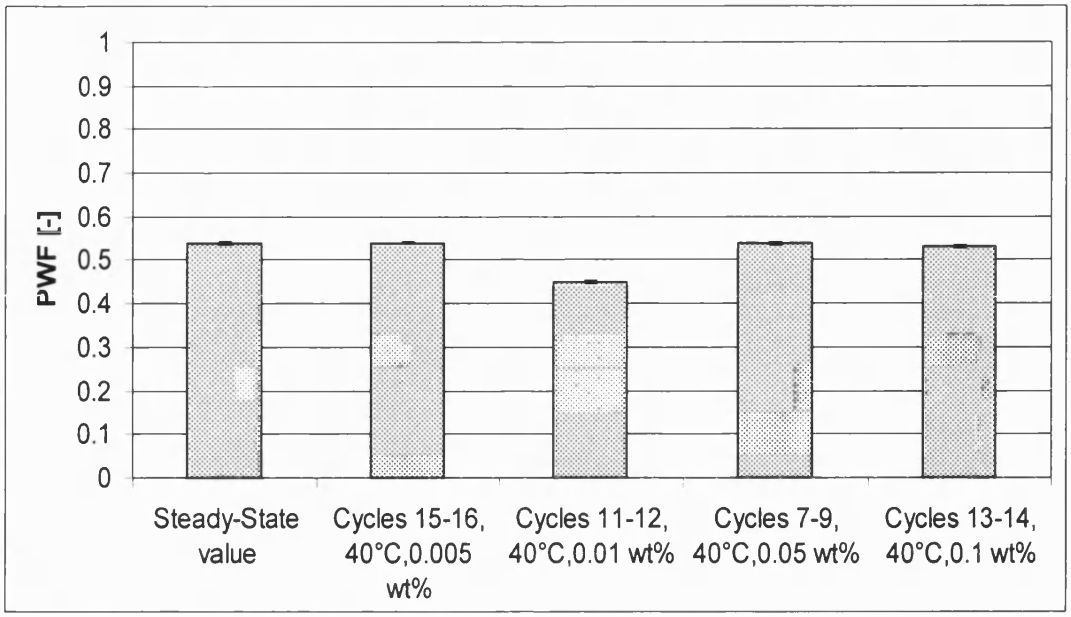


Figure 5.21(b): Pure water flux recovery after cleaning of multiple VHV-S fouled RC membrane at different Ultrasil 11 solution concentrations (Protocol 2; steady state = average from cycles 7,8,10; conditions 0.05wt% Ultrasil 11 , 40°C, 1.9 ms^{-1}).

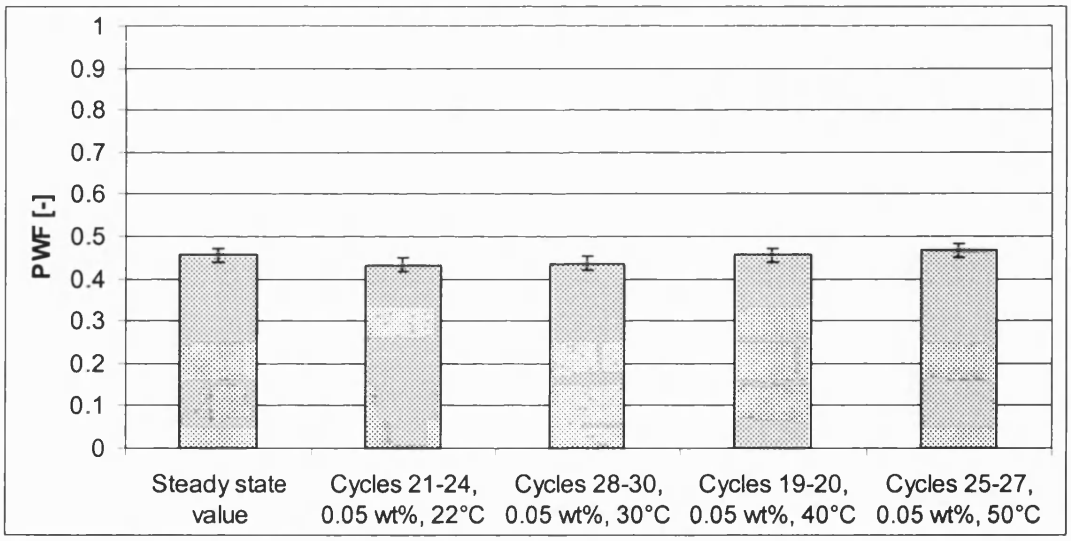


Figure 5.22(a): Pure water flux recovery after cleaning of multiple VHV-S fouled RC membrane at different NaOH solution temperatures (Protocol 2; steady state = average from cycles 19-20; conditions 0.05wt% NaOH, 40°C, 1.9 ms^{-1}).

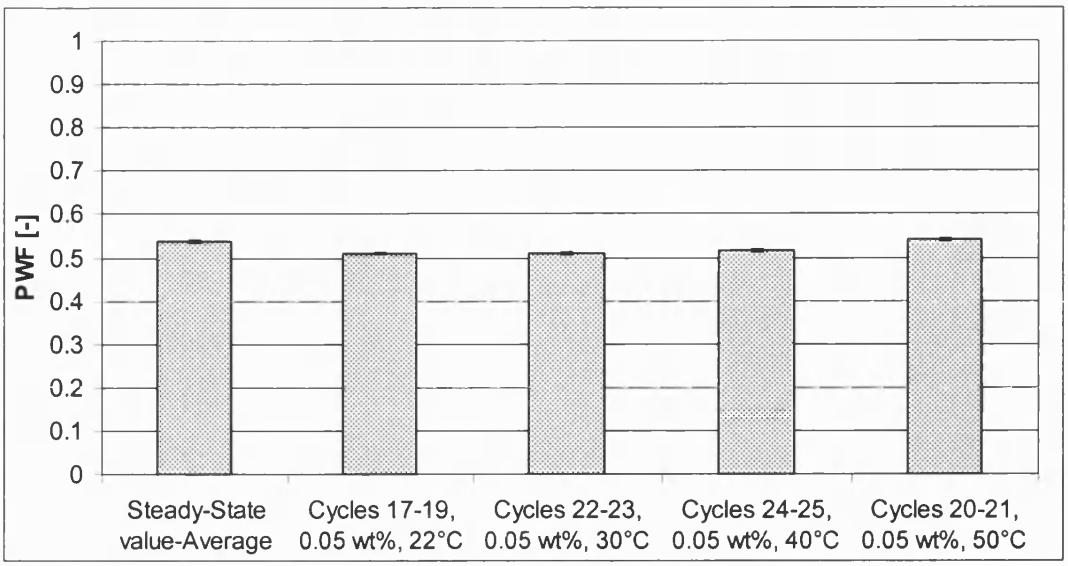


Figure 5.22(b): Pure water flux recovery after cleaning of multiple VHV-S fouled RC membrane at different Ultrasil 11 solution temperatures (Protocol 2; steady state = average from cycles 7,8,10; conditions 0.05wt% Ultrasil 11, 40°C, 1.9 ms^{-1}).

In Figure 5.21(a) the pure water flux is displayed after cleaning of multiple fouled RC membrane with different NaOH solution concentrations. Change of concentration has no impact and decline is due to progressing number of cycles. For *Ultrasil 11* the picture is somewhat different (Figure 5.21(b)). A change of concentration does not show any difference in performance either, but at least the small decline, as it can be seen for NaOH cleaning, is prevented when the membrane is cleaned with *Ultrasil 11*. This is most likely due to the increasing hydrophobicity of the membrane due to foulant attachment and increasing attraction of surfactants, hence buffering the decline when the number of cycles are progressing.

A change of solution temperature has a significant impact (see Figure 5.22 a-b). Not only is the decline from the previous cycles stopped, the flux improves steadily with increasing temperatures. The reader should bear in mind that the histograms display average values of three consecutive cycles, and examination of Figures 5.9(a) and (b) reveals, that these consecutive cycles show an increasing or decreasing slope, in particular the corresponding product flux values seen in Figure 5.7(a) and (b).

For alteration of *Ultrasil 11* solution temperatures, the picture is different. Since the introduction of surfactants has already started at previous cycles, a significant further

impact of temperature changes can not be seen. The performance improvements remain small.

5.4 Summary

Cleaning is a difficult area to study. The problem is complex and many parameters may influence the process. Some important parameters cannot be investigated directly, and to a certain extent the process may be treated as a black box. Any attempt to explain performance behaviour must be based upon sound evidence. Such evidence must come from a range of analytical tools; each of them should use a different physical principal to establish relationships. Only if all analytical data fit together and result in trends should one draw conclusions.

This strategy was applied in this study and found to be a good method to resolve complex problems.

The aim of this analysis part was to identify the relationship between membrane, foulants and cleaner and how these dependencies can influence the performance of filtration over both the short and the long term. This was done by studying the filtration performance, such as measurement of product and pure water fluxes as well as retention behaviour. Added to the fhe filtration results were indirect analytical measurements to determine important surface properties, such as wettability and surface charge. These measurements were followed by qualification and quantification of the foulants by extraction and FTIR analysis.

The results in this chapter revealed that there is a big influence of membrane material upon the fouling and cleaning behaviour. This relationship leads to different short and long term behaviour depending upon which membrane materials and cleaning agents were used. In fact, these dependencies are so big that the question of membrane material choice and cleaning agent becomes the one which determines the whole viability of the process.

A detailed summary of the results and the conclusions drawn from these results will follow in the next chapter.

Chapter 6

Conclusions

&

Future

Work

6 Introduction

The aim of the project was to study the relationship between membranes, fouling deposits and cleaning agents, as well as the influence of multiple fouling and cleaning cycles upon the system performance.

To reveal dependencies, membranes of different materials were fouled and cleaned with a formulated cleaning agent *P3 Ultrasil 11*. Since the major component of *Ultrasil 11* is sodium hydroxide, the experiments were repeated with NaOH, in order to understand the function of the ingredients of *Ultrasil 11* and how they interact over time with the membrane and fouling material.

Fouling and cleaning are complex phenomena, where many parameters influence the results. Proving a certain hypothesis is therefore difficult with only one analytical tool. To overcome this obstacle, different parameters were measured and different tools were used in order to see if the results match a global trend.

The results confirm that this approach works well. Clear trends were uncovered, which reveals that cleaning and the choice of membrane material determine the effectiveness of the filtration process. Major results are:

- Membrane material determines the type of fouling (hydrophobic or hydrophilic molecules). The degree of fouling depends on the nature of the feed material in relation to the membrane material.
- Membrane material determines the type of cleaning to be used. This is valid for all cleaning agents with a tendency to adsorb on surfaces, like surfactants.
- The efficiency of cleaning agents depends strongly on the surface hydrophobicity and the type of fouling material. The surface hydrophobicity can change over time and the effect of certain cleaning agents is strongly time dependent.
- Fouled and cleaned membranes reach a quasi steady state after 5-15 cycles, which is dependent on the membrane material and cleaning agents used. This state, when fouling and cleaning are in equilibrium, cannot be broken by

changes in cleaning agent concentration, but a temperature change has an impact.

The analytical tools used, in particular FTIR and zeta-potential, proved to be very useful in understanding the small changes occurring due to fouling and cleaning. FTIR has been successfully used so far only for investigations of pristine membranes, for once and for long term fouled membranes. But the tools prove to be good for detecting small changes and hence it is plausible that both tools can be used for online investigations.

In the next pages a critical review of all results will be given, including the use of the experimental rig in this study. This will then be used to draw conclusions and to give an outlook on future research work on fouling and chemical cleaning.

6.1 The experimental rig

The rig is a compromise between scientific and economical considerations, functionality and safety. It is tailor made built for the use of real feed materials and larger volumes (>50 L) than those one would use for model solutions. The general advice is that the feed volume should exceed the maximum permeate flow by a large amount, in order to minimise the volume reduction. It was pointed out by *Tsapiuk et al.* 2002 that any volume reduction, which differs from zero, can alter the retention behaviour. Therefore, the volume of feed was kept rather large in comparison to permeate flow (15 L to ~0.5 L/5 min.) and the permeate was recycled every 5 min.

The rig worked well and delivered accurate results. This became clear, when the number of cycles had progressed and the steady state was reached. The steady state for each cycle was established at almost exactly the same value as the previous one, varying only with a very small degree, which was due to the natural deterioration due to progressing number of cycles rather than due to the experimental rig itself.

The rig follows a straightforward design, which makes it flexible and easy to operate. Such a design was thought to be necessary to overcome the large amount of experiments/number of cycles needed for the study. A disadvantage is the relativly high area of shared pipes. This proved to be a problem, when wanting to determine the removal of foulants from the membrane surface. It was established that the removal from the pipe and heat exchanger walls contributed about 1/3 of the total removal during cleaning. But this value has a high standard deviation. Therefore, the precise amount of foulants removed from the membrane is considered difficult to determine. In addition, the kinetics of deposit removal from the pipework and the membrane surface were not determined. This might affect the results as well. However, the mixture of foulants from pipes and membrane within the feed solution does not influence the measurement of the pure water flux recovery, which gives a good indication about the removal. Therefore, the rig served the purpose of this project very well, including the self designed module. In future, a flat-sheet membrane module in sandwich design would be advisable. Such modules are commercially available, but unfortunately have unpredictable and uncharacterised geometries of the flow channels leading to non uniform shear-stress distributions.

6.2 Filtration results

The experimental results including product flux and pure water flux measurements as well as retention were obtained according to two different protocols. The characteristics of the first protocol was that the chemical wash was carried out at ambient temperature and the glycerine removal was incomplete. The second protocol was at hot temperatures (60°C) and included a complete removal of glycerine.

6.2.1 Summary and conclusions for cold washing (1st protocol)

In this study only hydrophobic membranes made of polyethersulphone or polysulphone were used. For sodium hydroxide cleaning of PES membrane a decline could be seen for the first 7 cycles. From the 8th cycle onwards a steady-state is established. It is most likely that sodium ions react with the negatively

charged functional groups of the foulants and become more hydrophobic, hence attracting even more foulants until the surface is saturated.

For *Ultrasil 11* cleaning of PES membranes an initial decline cannot be seen to such a degree as it can be seen when cleaning with sodium hydroxide. The EDTA present in *Ultrasil 11* keeps the metal ions away from the functional groups of deposits, hence rendering them charged as can be seen from the zeta-potential results. Furthermore, surfactants from *Ultrasil 11* become attached to the membrane surface, keeping it more hydrophilic than would otherwise be the case. But this attachment is limited at ambient temperature cleaning.

For the PSf membrane it becomes clear that the surface roughness plays a major role in the fouling mechanism. Here, the pore size and distribution are more important for determining flux decline than the membrane material itself. There is no chemical modification of the membranes indicated by the zeta-potential, whether cleaned with NaOH or *Ultrasil 11*. These results show, in contrast to those seen for the PES membrane, that surface chemistry is not the dominant force determining membrane separation and flux performance.

For NaOH cleaning of PES membranes the PWF results are a confirmation of the product flux results. For *Ultrasil 11* cleaning it becomes obvious that when the effects of minor components start to influence performance it leads to no further decline in flux.

PWF is very helpful in confirming trends already seen for the product flux. Beyond that it reveals more details about the fouling and cleaning mechanism and their interaction.

6.2.1.1 Influence of Concentration and Temperature

The influence of concentration and temperature during cleaning was determined with the help of the pure water flux of the pristine membrane as a reference value.

When the PES and PSf membranes are once fouled and cleaned with different NaOH concentrations, the cleaning effect is more significant for the PSf membrane. This is probably due to the smaller pore size, which makes the PSf

membrane more vulnerable to complete pore blocking. Hence fouling removal affects the PWF recovery more strongly. When PES and PSf membranes are once fouled and cleaned with different *Ultrasil 11* concentrations, the surfactant adsorption for PES and the effect on PWF recovery is much bigger than what is seen for PSf. This is understandable as PES is more hydrophobic and has a higher porosity, hence surface area in comparison to PSf.

When temperature is increased for the PES and PSf membrane cleaning, the PWF recovers to a value above that seen for the pristine membrane. For NaOH cleaning, this is due to the additional and complete glycerine removal, for *Ultrasil 11* cleaning, the surfactant adsorption also plays a role.

- **For cleaning of once fouled membranes, the morphology of the membrane, such as surface roughness, pore size and distribution determine the performance initially. When the surface area increases alongside a higher pore size distribution, the surface chemistry becomes more important in determining the cleaning performance, in particular when surfactants are used.**
- **Surfactants do not only help to solubilise foulants, their importance appears to be more in interacting with the membrane, by becoming adsorbed to the surface and by changing the hydrophobicity.**

6.2.2 Glycerine removal

After 20 min. at 60°C and 1 bar in dead-end mode pure water filtration, approximately 80% of the total amount of glycerine is removed from the pristine membrane (PES and PSf). One would expect that such an amount of removal would be sufficient and that the remaining glycerine would not have any impact on fouling. But this is not the case. Results show clearly that membranes, which are conditioned for 15 minute at ambient temperature perform better for the first 1.5 hours than fully conditioned membranes. Until it is completely removed the remaining glycerine forms a hydrophilic layer, which gives some protection towards adsorption of hydrophobic foulants.

- **Glycerine removal is far more difficult to achieve than initially thought. Although glycerine is highly water soluble, it can remain in the smallest pores, if the membrane is not washed with pure water at high temperatures for a long enough time. If glycerine remains, it will serve as a hydrophilic layer preventing fouling adsorption. For accurate laboratory work glycerine needs to be removed, otherwise it can influence the results.**

6.2.3 Summary and conclusions for hot washing

With the hot wash protocol (protocol 2), the same polyethersulphone membrane as in the cold wash protocol (protocol 1) was used, but also hydrophilic regenerated cellulose membranes were tested at an intermediate temperature. When PES membrane is washed with NaOH at hot temperatures the same trend appears as already seen for cold wash over many cycles. What is different is the total degree of recovery for each single cycle, which is higher for hot wash.

When the PES membrane was cleaned with *Ultrasil 11* at hot temperatures the results were very different from those of the cold wash. For the cold wash there was an initial decline until cycle 7, whereas for hot wash the flux remained high at the level of the pristine membrane and did not decline. The hot cleaning temperature supports the attachment of surfactants; hence the surface remains more hydrophilic and will serve as a protection repelling hydrophobic foulants. Once again, the pure water flux confirms the results for the product flux, and provides a more detailed picture of what is happening at the surface.

When the RC membrane is cleaned with NaOH it shows a similar flux decline as was seen for the PES membrane, but in total not as severe. This is most likely due to the much greater hydrophilicity of the membrane, hence its tendency to repel hydrophobic foulants.

When cleaned with *Ultrasil 11*, there is also an initial decline in performance. This is due to the hydrophilicity of the membrane, giving the surfactants of *Ultrasil 11* no chance to adsorb. This slowly starts to happen when the membrane surface becomes more and more hydrophobic with increasing number of fouling cycles, hence the performance improves again.

The PWF values for cleaning of RC membrane confirm the results of the product flux.

- **When hydrophobic membranes are cleaned with hot single formulated cleaning solutions the total degree of cleaning is increased for each single cycle in comparison with cold cleaning. But the overall trend seen over many cycles are the same for both types of cleaning. When multiple formulated agents are used for hydrophobic membranes, the temperature of the cleaning solution plays a big role for both the single cycle and the trend over many cycles. High temperatures improve the interaction of cleaning agents with the membrane (e.g. surfactants) and with foulants (e.g. EDTA).**
- **For hydrophilic membranes and the single (only NaOH) formulated cleaning solution, the trend over many cycles is similar to that seen for hydrophobic membranes. But in total it is not as severe, due to the fact that there are not so many foulants accumulating on hydrophobic membranes (e.g. PES). When multiple formulated cleaning agents are used, the ingredients start to interact with the surface (e.g. surfactants) as soon as enough fouling material has built up, making it more hydrophobic. Therefore, it would probably be advisable to use formulated agents only at a later stage of the membranes life-cycle.**

6.2.3.1 Retention

When the PES membrane is cleaned with NaOH the retention never reaches a steady-state, as was seen for the product flux and the PWF. This is the ultimate indication that fouling material is building up and that the pores are getting narrower, hence increasing retention. For *Ultrasil 11* cleaning retention does not increase, proving that the removal of foulants is considerable, and that a protective hydrophilic layer of surfactants is building up making further attachment of foulants much more difficult.

For RC membrane cleaning, NaOH does not have such a significant effect on retention as it has on PES membranes. The increase is much smaller, which is simply due to the small total amount of foulants attaching on the membrane surface. But fouling of even very small amounts onto the membrane seems to

dramatically change the hydrophobicity and therefore the product and the pure water flux values.

For *Ultrasil 11* cleaning, there is no increase at all in retention. After many cycles there can be even a slight decline. Once again, there is hardly any fouling and if nonionic surfactants start to accumulate on the surface retention starts to increase.

- **The retention gives very valuable information about the fouling and the cleaning process beyond that what can only be retrieved from product and pure water flux measurements. For instance, although the product and pure water fluxes are stable, retention continues to increase when cleaned with NaOH, which clearly indicates that fouling is still progressing. Therefore, without retention values, one could come to the wrong conclusions.**

6.2.3.2 Cleaning efficiency

Valuable information can be retrieved from PWF developments before and after rinsing and after washing with a chemical-cleaning agent.

The chemical wash is more effective during the initial decline phase, for the PES membrane cleaned with sodium hydroxide this is up to fouling cycle 7. In this region, the wash is about 1/3 more effective than it is in steady-state. Also, the choice of cleaning agent influences the performance of the rinsing. When cleaned with NaOH, the rinsing flux drops from 20 kg $m^{-2}h^{-1}$ for the 1^{st} cycle (virgin membrane) to 10 kg $m^{-2}h^{-1}$ for all the rest of the cycles. For *Ultrasil 11* cleaning the attachment of surfactants enhances the rinsing, increasing both PWF values before and after rinsing.

For cleaning of RC membrane with NaOH, a cleaning effect exists, when looking at the first 5 cycles. Cleaning is still significant then, even though the amount of fouling is much smaller in comparison to that of PES membrane and the cleaning agent amount used is less due to the RC material restriction for pH and temperature. But when the steady state is reached the cleaning effect is almost reduced to zero and in fact insignificant.

Ultrasil 11 does not perform better than NaOH when cleaning over a short term. Only when the cycle number is progressing and the surface becomes more

hydrophilic, surfactants get attached to the surface making the membrane more hydrophilic. This then improves the rinsing performance. *Ultrasil 11* reported in this investigation is a poor cleaning agent for hydrophilic membranes as many ingredients such as EDTA have no significant effect until more deposit becomes attached to the surface in the long run.

- **Valuable information can be retrieved from PWF developments before and after rinsing and after washing with a chemical-cleaning agent. The completely different performance of chemical cleaning during the initial stages of the membrane life-cycle in comparison to the stage when steady-state is reached, proves that very different cleaning mechanisms are involved.**
- **The cleaning performance of NaOH on hydrophobic membranes deteriorates with progressing cycle number. With *Ultrasil 11, the* performance remains constant. If NaOH is used on hydrophilic membranes the performance also deteriorates. For Ultrasil 11 a slight improvement can be seen over many cycles, due to surfactant attachment.**
- **The rinsing performance is altered when different cleaning agents are used, for instance NaOH reduces the effect of rinsing and *Ultrasil 11* greatly improves the effect of rinsing upon subsequent flux values.**

6.3 Impact of cleaning agent concentration and solution temperature upon long term performance

For membranes, which were long time tested, the virgin membrane flux was substituted by the flux at steady-state, in order to calculate the relative flux decline Jn/Jo. The steady-state value proved to be an excellent reference value.

Product Flux

For PES membranes cleaned using NaOH, concentration change has virtually no impact on recovery within the range tested and cannot even prevent the natural small decline over progressing cycles. In contrast, temperature has a big impact.

For *Ultrasil 11* cleaning the effect of cleaning agent concentration is not important upon the steady-state flux value over the range tested and has virtually no impact. It either appears that this is true also for temperature, but pure water flux development does not support that. Changes of product flux become visible only after two or more cycles. This is because changes in hydrophilicity have a particular impact on water flux but to a less extent on the product flux.

When long term fouled RC membrane is cleaned with different NaOH or *Ultrasil 11* concentrations no impact upon the steady-state flux values can be seen whatsoever over the range tested. When temperature is changed during NaOH cleaning, it has a clear impact, but in total the change remains little, even when looking at the difference between 22°C and 50°C. When cleaning with *Ultrasil 11* at different solution temperatures the effect of surfactant adsorption supersedes the effect of deposit dissociation caused by elevated temperatures, hence the recovery remains rather constant.

Pure water Flux (PWF)

For the PES membrane and NaOH cleaning at different solution temperatures a clear impact can be seen. The recovery values due to different solution temperatures are almost proportional to the temperature increase. The same is valid for *Ultrasil 11* cleaning at different temperatures. The main difference between the performance of NaOH and *Ultrasil 11* is whilst for NaOH the PWF recovery remains below the value of the virgin membrane, the value for *Ultrasil 11* raises far above it.

Multiple fouled RC membranes cleaned with different NaOH solution concentrations show no change in performance and decline is due to increasing number of cycles. For *Ultrasil 11* the picture is somewhat different. Changes in concentration do not show any difference in performance, however the small decline seen for NaOH cleaning is prevented when cleaned with *Ultrasil 11*. This is most likely due to the increasing hydrophobicity of the membrane and increasing attraction of surfactants, hence buffering the decline when the number of cycles are progressing.

A change of NaOH solution temperature has a significant impact upon the multiple fouled RC membrane. Not only is the decline seen from the previous cycles stopped, it improves the flux steadily with increasing temperatures. For alteration of *Ultrasil 11* solution temperatures, the picture is different. Since the presence of surfactants has already started from the previous cycles, a significant further impact of temperature changes can not be seen. The performance improvements remain small.

- **Long term fouled membranes follow a different cleaning mechanism than once-fouled membranes. For the concentration range tested (0.001-1.0 wt%), changes in concentration do not have any effect on pure water or product flux, whether hydrophobic or hydrophilic membranes are used and no matter if cleaned with NaOH or *Ultrasil 11.***
- **When the cleaning solution temperature is varied the impact on recovery is big and almost proportional to the degree of temperature change, in particular for PWF. For the product flux the improvement is less significant and for hydrophilic RC membrane the improvement due to higher temperatures is superseded by the attachment of surfactants.**
- **The remarkable difference in performance between short and long term fouled membranes should lead to different cleaning strategies over the short and long term for different membrane hydrophobicities.**

6.4 Analytical results

The analytical results deal with the question of what is happening on the membrane surface and/or in the pores. These results give information about the quality and quantity of foulants involved and the quality and quantity of interaction of cleaning agents with membrane material and foulants. They complement the results from the filtration experiments and conclusions drawn from the analytical data support the conclusions from the filtration results.

6.4.1 Extraction results

More hydrophobic fouling material was found on the PES membrane in comparison with the PSf membrane. This is due to the slightly higher hydrophobicity and higher surface area of PSf membranes in comparison with the PES membranes. In addition, the type of adsorbed foulants will be different when surface hydrophobicity changes. The main foulants for both membranes are fatty acids, resin acids, lignans, and most likely the lignosulphonates.

6.4.2 Contact angle results

The preservation agent glycerine serves as a temporary protective layer. Any glycerine remaining on the membrane makes the surface more hydrophilic. The contact angle measurements are a good tool to detect interaction of cleaning agent with the membrane and fouling material. Such interactions result in a change of wettability, hence different contact angles. However, hysteresis effects due to different surface roughness can be large and result in large deviations. Therefore, small differences in wettabilty do not necessarily mean different hydrophobicity of the material. This was seen in this study for the pristine PES and PSf membrane. According to literature the PSf is more hydrophobic than PES, but contact angles gave the opposite conclusion. The rather high surface roughness of PSf membrane in contrast to the PES membrane could have caused this result.

6.4.3 ATR-FTIR results

ATR-FTIR was found to be very useful in detecting even small changes of fouling layer removal/adsorption and determining the type of interaction with the membrane. On the other hand because of the overlapping of peaks it was troublesome to accurately determine functional groups of polymer, fouling material and cleaning agents with the help of FTIR spectra and hence class them to specific substances. It is possible but for foulant substances identification extraction is here much better and delivers reliable results.

FTIR made it possible to prove that glycerine was removed.

Examination of the final IR data makes clear what is happening on the membrane surface. Cleaning using NaOH on hydrophobic PES membranes leads to the removal of foulants alone. A trend is established with an increase (fouling) and decrease (cleaning) of foulants concentrations and margins getting smaller and smaller as cycles progress until a quasi-steady state is reached.

When the PES membranes are cleaned with *Ultrasil 11*, a recovery in terms of peak height due to cleaning cannot be seen. This does not indicate that no removal of foulants has taken place. Rather it proves the strong adsorption of surfactants on the membrane surface, when cleaned with *Ultrasil 11.*

For the RC membrane the peak height changes are identical no matter if cleaned with NaOH or Ultrasil 11 for the concentration range tested. That means there is no difference in performance for NaOH and *Ultrasil 11* detectable. This result is confirmed by the peak-height values over long term, which also do not show any difference. This contradicts the pure water flux results for RC membrane when cleaned with Ultrasil 11. Surfactants become adsorbed onto the RC membrane as the number of cycles progresses, hence increasing the hydrophobicity. In the FTIR spectra these surfactants appear as a fouling layer and hence these surfaces seem to be fouled as much as RC membrane cleaned with NaOH.

- **FTIR is an excellent, non-invasive tool to follow fouling accumulation and even small changes can be detected. In this study FTIR confirms the findings from the filtration experiments. However, it is troublesome to use FTIR to determine the type of fouling and the specific molecules involved. Therefore, FTIR results need to be supported by other results, which help to interpret IR-bands and peaks.**

6.4.4 Zeta-potential results

Zeta-potential is another tool to retrieve more information on the chemistry when membrane surfaces are fouled and cleaned. In addition, the values will give information about the foulant cleaner interaction.

6.4.4.1 Zeta-potential results for protocol 1

If the membranes are once-fouled the influence of the polymer disappears and the zeta-potential completely changes in comparison with that of the virgin membrane. For the PES membrane, cleaning with NaOH or *Ultrasil 11* has a measurable impact on the zeta-potential, and therefore provides a clear indication of foulant-cleaner interaction. NaOH reduces the potential by about a half. With *Ultrasil 11* cleaning the potential remains almost at the value of the once fouled membrane. For the PSf membrane, no change in zeta-potential can be detected. Here, other cleaning and fouling mechanisms exist, and physical fouling (complete pore blocking) and physical cleaning mechanisms (removal of foulants) seem to be dominant and determining fouling and cleaning performance.

6.4.4.2 Zeta-potential results for protocol 2

The results confirm what was already described with the FTIR results. When cleaned with NaOH a trend is established with an increase (fouling) and decrease (cleaning) of zeta-potential, with margins getting smaller and smaller as cycles progress until a quasi steady-state is reached. For *Ultrasil 11* cleaning the zeta-potential does not recover as much as it can be seen for NaOH and stays rather negative with a declining trend. This is due to the effect of the EDTA and surfactants. The trends over two cycles fit to the results over many cycles, with Ultrasil 11 remaining a more negative zeta-potential than what was found for NaOH.

For RC membranes the results are rather different to those found for the much more hydrophobic PES membranes. When fouled once, the zeta-potential increases quite significantly to almost twice as negative as that of the virgin membrane. Cleaning has almost no impact upon the zeta-potential. It appears that fouling does indeed occur, this does not physically block the pores, but starts to change the hydrophilicity dramatically, hence product and PWF are both declining in the initial stages of the membrane lifetime. Surfactants do not have an impact and do not get adsorbed, since the membrane is too hydrophilic. This starts only when the number of cycles progresses and the membrane becomes more fouled, hence becomes more hydrophobic.

- **Zeta-potential analysis is an excellent tool to establish if surface chemistry plays a part in influencing filtration performance and to identify the type of foulant-cleaner interaction. It is very useful for the support of analytical data.**

6.5 Future work and recommendations

During the work on this project and as feedback received from conferences and meetings, other researchers commented upon the insular nature of this research work. Their argument was that my results would only be applicable for wood pulp and even then only for a particular kind of wood pulp, in this case spent sulphite liquor. This argument cannot be completely rejected. However, wood pulp contains a broad range of foulants, which are important in many other feed streams, such as ground and surface water (e.g. humic acids), feeds from the food industry (e.g. phenols from fruit juices, wine) and in general chemical industry (e.g. fatty acids, phenols). Besides this, general phenomena were studied, which appear in all membrane processes and the interpretation of the results is not based on only one model foulant. An example for this is the tendency of hydrophobic molecules to adsorb on hydrophobic surfaces different in quantity and quality than on hydrophilic surfaces. This is valid for all substances, no matter which particular molecule it is.

Nevertheless, it would be of great help if some key experiments were carried out to confirm the results obtained for wood pulp. The feed material of interest should be of a different nature in order to determine the general applicability of the results determined this far. Besides substances of a wood origin other material could be used, such as proteins, starch and pectin, oils and fats.

In future, a multivariate analysis needs to be implemented in order to overcome the vast amount of experimental work. If this is not done complex problems such as the fouling and cleaning problem cannot be tackled successfully. Another reason for this approach is the fact that many parameters are correlated with each other, and cannot be investigated experimentally independently from each other, by varying one parameter while maintaining others constant. Applying

multivariate analysis is in itself difficult and needs training. Using it for tackling actual research problems demands deep knowledge of both, the statistical analysis tools and understanding of the scientific problem. The danger is that for many problems the use of statistical analysis is not appropriate and would be misleading, for others it is helpful. For future research in fouling and cleaning it needs to be established, for which particular field statistical analysis is appropriate and where not.

A big field of interest is also the question if the performance can be altered with a change of cleaning agent over time. This is most likely and has a potential for big savings in material and cost. For *Ultrasil 11* it appears that surfactants are only useful for the first 5 cycles on hydrophobic membranes, where they get attached to the surface. After that *Ultrasil 11* can be substituted with a much cheaper single formulated agent. For hydrophilic membranes the use of *Ultrasil 11* is appropriate only after the membrane has become more hydrophobic due to fouling. These sorts of experiments are time intensive and some thoughts should be given on how to improve the experimental set-up in order to speed up the process of sampling treated membranes after high numbers of cycles. One possibility is here the use of a flat sheet module with up to 10 sheets in series. With such a module long term experiments could be done quickly. In order to develop such a device the question must be answered, how pressure and volume reduction affects a particular fouling process, since there will be a pressure drop over such a big module and a large volume reduction. In relation to this the question must be answered how adsorption without any pressure affects the cleaning, and how additional pressure during fouling will alter the cleaning performance. From the results obtained in this study it appears that pressure during fouling is not responsible for the different degrees of removal during cleaning. It looks as if the fouling layer responsible for the long-term deterioration is building up just by adsorption and gets bigger until the polymeric membrane surface is saturated with the fouling molecules. When investigating this it must be considered that adsorption is possibly correlated to pressure and time of exposure and once again the use of statistical analysis here is important.

A very versatile tool was found in atomic force microscopy. The tool was used intensively, although the results are only partly presented in this thesis and can be found elsewhere, *Chukwuemeka* 2002. Unfortunately the full potential of this analytical tool was not used, mainly because of lack of time, since AFM is in general easy to use, but time consuming. But when used appropriately, surface energy changes can be determined accurately due to fouling and cleaning and at the same time pictures can be taken and surface roughness analysis be carried out. Beyond this, the cantilever can be attached with any sort of foulant, so that the adsorption force towards the membrane material can be determined accurately. All this can be carried out under the real conditions and therefore accurate data can be obtained from the real process. Due to these advantages, AFM should in future become an integral part of membrane research in our laboratory.

6.6 Final summary

The investigation is the first scientific long term study of its kind, combining filtration data of fouling and cleaning with chemical analysis methods.

It has shown that surface roughness and as a result of it the membrane area is the dominant factor influencing fouling. The higher the roughness the bigger the influence of that factor on fouling. If the roughness decreases, the membrane material becomes more influential, with its material specific short range forces, such as Van der-Waals, ion-exchange and water bond forces. Therefore fouling cannot simply be avoided by reducing surface roughness, but a reduction helps to reduce complete pore blocking. For membranes, where the electrostatic forces play the dominant role, the chemical cleaning becomes an important process step, in order to influence the filtration performance. On membranes with high surface area and low roughness, the electrostatic forces can be influenced by the correct choice of cleaning agent, and can have a synergistic effect. As a result of the right cleaning, this can maintain the flux and retention at a certain level, where without or with false chemical cleaning, the flux had dropped and the retention had risen. For membranes, where electrostatic forces play the dominant role for the separation performance, the choice of cleaning agent will determine the entire

economy of the pocess, since it can influence the separation performance over short and long term significantly.

ATR-FTIR, zeta-potential measurements and contact angle are excellent tools to show that interactions between adsorbed foulants and cleaning agent exists. Particular IR analysis has a great potential as non-invasive tool.

Until today, there is no membrane commercially available without fouling tendencies. Therefore, understanding the fouling and cleaning mechanism is of crucial importance, where chemical cleaning remains until today the primary choice to maintain filtration performance. In this study it was shown that the fouling layer can be influenced by cleaning on the level of electrostatic interactions. In this way it depends on the membrane material and the used cleaning agents. In the positive case a synergistic effect can be achieved and subsequent fouling cycles are influenced by the cleaning. The result is important, because it shows that cleaning is not just about an independent removal of fouling substances from the surface. Cleaning affects also the nature of the remaining deposit and hence influences subsequent cycles. In future this will alter cleaning strategies.

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Appendix

8.1 ATR-FTIR peak heights for selected peaks

Table 8.1: Peak heights for virgin and VHV-S fouled and sodium hydroxide cleaned PES membranes. Corresponds to figure 4.10

Membrane-Fouling and Cleaning State	Wavenumber 1667 cm^{-1}	1280 cm^{-1}	850 cm^{-1}	780 cm^{-1}	750 cm^{-1}
PES-Virgin					
1st sheet	0.64	0.75	0.68	0.30	0.51
2nd sheet	0.64	0.74	0.67	0.30	0.51
3rd sheet	0.76	0.72	0.63	0.29	0.57
Average	0.68	0.74	0.66	0.30	0.53
StDev	0.07	0.02	0.03	0.01	0.03
PES-1 x fouled					
1st sheet	0.54	0.68	0.57	0.23	0.41
2nd sheet	0.54	0.68	0.57	0.23	0.42
3rd sheet	0.56	0.67	0.56	0.23	
Average	0.55	0.68	0.57	0.23	0.42
StDev	0.01	0.01	0.01	0.00	0.01
PES- 1f/1c-NaOH					
1st sheet	0.53				
2nd sheet	0.58	0.70	0.65	0.28	0.48
3rd sheet					
Average	0.56	0.70	0.65	0.28	0.48
StDev	0.04				
PES- 2f/1c-NaOH					
1st sheet	0.53	0.70	0.55	0.22	0.39
2nd sheet	0.51	0.67	0.55	0.20	0.39
3rd sheet		0.66	0.55	0.23	
Average	0.52	0.68	0.55	0.22	0.39
StDev	0.01	0.02	0.00	0.02	0.00
PES- 2f/2c-NaOH					
1st sheet	0.53	0.65	0.53	0.20	0.39
2nd sheet	0.54	0.67	0.57	0.22	0.41

3rd sheet		0.69	0.56	0.23	
Average	0.54	0.67	0.55	0.22	0.40
StDev	0.01	0.02	0.02	0.02	0.01
PES- 20f/20c-NaOH					
1st sheet	0.25	0.38	0.27	0.10	0.20
2nd sheet	0.31	0.40	0.31	0.13	0.24
3rd sheet		0.33	0.30	0.10	0.23
Average	0.28	0.37	0.29	0.11	0.22
StDev	0.04	0.04	0.02	0.02	0.02

Table 8.2: Peak heights for virgin and VHV-S fouled and Ultrasil 11 cleaned PES membranes. Corresponds to figure 4.12.

Membrane-Fouling and Cleaning State	**Wavenumber**				
	1667 cm^{-1}	1280 cm^{-1}	850 cm^{-1}	780 cm^{-1}	750 cm^{-1}
PES-Virgin					
1st sheet	0.64	0.70	0.68	0.30	0.51
2nd sheet	0.64	0.75	0.68	0.30	0.51
3rd sheet	0.64	0.75	0.68	0.30	0.51
Average	0.64	0.73	0.68	0.30	0.51
StDev	0.00	0.03	0.00	0.00	0.00
PES-1 x fouled					
1st sheet	0.54	0.63	0.58	0.23	0.41
2nd sheet	0.55	0.68	0.57	0.23	0.41
3rd sheet	0.55	0.68	0.57	0.23	0.41
Average	0.55	0.66	0.57	0.23	0.41
StDev	0.01	0.03	0.01	0.00	0.00
PES- 1f/1c-Ultrasil 11					
1st sheet	0.34	0.54	0.52	0.19	0.37
2nd sheet	0.30	0.51	0.44	0.15	0.32
3rd sheet	0.40	0.48	0.43	0.18	0.32
Average	0.35	0.51	0.46	0.17	0.34

StDev	0.05	0.03	0.05	0.02	0.03
PES- 2f/1c-Ulrasil 11					
1st sheet			0.36	0.12	0.28
2nd sheet	0.38	0.57		0.18	0.34
3rd sheet	0.46	0.48	0.40	0.15	0.30
Average	0.42	0.53	0.38	0.15	0.31
StDev	0.06	0.06	0.03	0.03	0.03
PES- 2f/2c-Ultrasil 11					
1st sheet				0.12	0.28
2nd sheet	0.35	0.50	0.46	0.15	0.33
3rd sheet	0.46	0.58	0.50	0.17	0.37
Average	0.41	0.54	0.48	0.15	0.33
StDev	0.08	0.06	0.03	0.03	0.05
PES- 14f/14c-Ultrasil 11					
1st sheet	0.23	0.36	0.31	0.12	0.23
2nd sheet	0.25	0.42	0.38	0.13	0.27
3rd sheet		0.43	0.38	0.15	0.28
Average	0.24	0.40	0.36	0.13	0.26
StDev	0.01	0.04	0.04	0.02	0.03

Table 8.3: Peak heights for virgin and VHV-S fouled and NaOH cleaned RC membranes. Corresponds to figure 4.14.

Membrane-Fouling and Cleaning State	Wavenumber		
	1725 cm^{-1}	1350 cm^{-1}	1220 cm^{-1}
RC-Virgin			
1st sheet	0.66	0.49	0.75
2nd sheet			
3rd sheet	0.61	0.47	0.72
Average	0.64	0.48	0.74
StDev	0.04	0.01	0.02
RC-1 x fouled			
1st sheet	0.67	0.40	0.68
2nd sheet		0.28	0.60
3rd sheet	0.49	0.31	0.59
Average	0.58	0.33	0.62
StDev	0.13	0.06	0.05
RC- 1f/1c-NaOH			
1st sheet	0.26	0.21	0.40
2nd sheet	0.33	0.29	0.50
3rd sheet	0.37	0.27	0.45
Average	0.32	0.26	0.45
StDev	0.06	0.04	0.05
RC- 2f/1c-NaOH			
1st sheet	0.22	0.18	0.34
2nd sheet	0.31	0.28	0.45
3rd sheet	0.30	0.21	0.36
Average	0.28	0.22	0.38
StDev	0.05	0.05	0.06
RC- 2f/2c-NaOH			
1st sheet	0.22	0.23	0.35
2nd sheet	0.19	0.22	0.32
3rd sheet		0.25	0.36
Average	0.21	0.23	0.34

StDev	0.02	0.02	0.02
RC- 30f/30c-NaOH			
1st sheet	0.06	0.15	0.06
2nd sheet	0.03	0.14	0.05
3rd sheet		0.21	0.06
Average	0.05	0.17	0.06
StDev	0.02	0.04	0.01

Table 8.4: Peak heights for virgin and VHV-S fouled and Ultrasil 11 cleaned RC membranes. Corresponds to figure 4.16.

Membrane-Fouling and Cleaning State	**Wavenumber** 1725 cm^{-1}	1350 cm^{-1}	1220 cm^{-1}
RC-Virgin			
1st sheet	0.66	0.48	0.75
2nd sheet			
3rd sheet	0.66	0.49	0.72
Average	0.66	0.49	0.74
StDev	0.00	0.01	0.02
RC-1 x fouled			
1st sheet	0.67	0.40	0.68
2nd sheet			
3rd sheet	0.67	0.40	0.67
Average	0.67	0.40	0.68
StDev	0.00	0.00	0.01
RC- 1f/1c-Ultrasil 11			
1st sheet	0.45	0.32	0.56
2nd sheet		0.24	
3rd sheet			0.63
Average	0.45	0.28	0.60
StDev		0.06	0.05
RC- 2f/1c-Ulrasil 11			

1st sheet	0.50	0.31	0.51
2nd sheet			
3rd sheet	0.48	0.33	0.62
Average	0.49	0.32	0.57
StDev	0.01	0.01	0.08
RC- 2f/2c-Ultrasil 11			
1st sheet	0.23	0.23	0.36
2nd sheet	0.23	0.22	0.37
3rd sheet	0.30	0.21	0.32
Average	0.25	0.22	0.35
StDev	0.04	0.01	0.03
RC- 25f/25c-Ultrasil 11			
1st sheet	0.05	0.25	0.12
2nd sheet	0.07	0.16	0.07
3rd sheet	0.15	0.21	0.09
Average	0.09	0.21	0.09
StDev	0.05	0.05	0.03

8.2 Protocols in detail

The following protocol was developed in the 1st year of study: **Protocol 1**

1. **Conditioning:** the membranes were treated for 15 min at 22°C with 0.1wt% *Ultrasil 11:*

- PES: Transmembrane pressure (TMP) of 1.5 bar, a cross flow velocity (CFV) of 1.8 ms^{-1}, permeate valve open.
- PSf: TMP 1.0 bar, CFV 1.8 ms^{-1}, permeate valve open.

The system was drained and rinsed with RO water.

2. **Pure water flux measurements:** measured once the flux was steady under following conditions.

- PES: TMP 5.25 bar, CFV 2.7 ms^{-1}, open permeate valve.
- PSf: TMP 5.25 bar, CFV 2.7 ms^{-1}, open permeate valve.

The system was drained

3. **Fouling**: a fouling time of 90 minutes at 70°C was found most suitable and similar to industrial separation.

- PES: TMP 8.25 bar, CFV 2.7 ms^{-1}, open permeate valve.
- PSf: TMP 7.00 bar, CFV 2.7 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water.

4. **Rinsing:** to remove loose deposits on the membrane surface the system was rinsed for 15 min, at 22°C

- PES: TMP 1.5 bar, CFV 1.8 ms^{-1}, open permeate valve.
- PSf: TMP 1 bar, CFV 1.8 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water.

5. **Cleaning:** duration was 30 min, with 0.5 wt% NaOH or *Ultrasil 11* at 22°C

- Nadir: TMP 1.5 bar, CFV 1.8 ms^{-1}, open permeate valve.
- Osmonics: TMP 1.0 bar, CFV 1.8 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water and PWF was measured(see step 2)

The following protocol was developed during the 2nd year of study: **Protocol 2**

1. **Conditioning:** the membranes were treated for 90 min at 60°C (PES membrane) and 50°C (RC membrane) with pure water.

- PES: Transmembrane pressure (TMP) of 1 bar, a cross flow velocity (CFV) of 1.8 ms^{-1}, permeate valve open.
- RC: TMP 1.0 bar, CFV 1.8 ms^{-1}, permeate valve open.

The system was drained and rinsed with RO water.

2. **Pure water flux measurements:** measured once the flux and pH of permeate was steady under the following conditions.

- PES: TMP 1 bar, CFV 1.8 ms^{-1}, open permeate valve.
- RC: TMP 1 bar, CFV 1.8 ms^{-1}, open permeate valve.

The system was drained

3. **Fouling**: a fouling time of 120 minutes at 70°C (for PES membrane) and 40°C (for RC membrane) was found most suitable and similar to industrial separation.

- PES: TMP 7.00 bar, CFV 2.45 ms^{-1}, open permeate valve.
- RC: TMP 7.00 bar, CFV 2.45 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water and the PWF was taken (see step 2).

4. **Rinsing:** to remove loose deposits on the membrane surface the system was rinsed for 15 min, at 60°C for PES and 40°C for RC membrane

- PES: TMP 1.00 bar, CFV 1.8 ms^{-1}, open permeate valve.
- RC: TMP 1.00 bar, CFV 1.8 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water and the PWF was taken (see step2).

5. **Cleaning:** duration was 30 min, with 0.5 wt% NaOH or *Ultrasil 11* at 60°C for PES membrane or 40°C for RC membrane.

- PES: TMP 1.00 bar, CFV 1.8 ms^{-1}, open permeate valve.
- RC: TMP 1.00 bar, CFV 1.8 ms^{-1}, open permeate valve.

The system was drained and rinsed with RO water. and the PWF was taken (see step 2).

8.3 Calculation of linear velocity and Reynolds Number

The Reynolds number is defined as

$$\mathrm{Re} = \frac{d\,u\,\rho}{\mu} \qquad (8.1)$$

where d = diameter of channel (m)

u = average linear velocity $9ms^{-1}$)

ρ = Fluid density (kg m^{-3})

μ = Fluid dynamic viscosity (kg $m^{-1}s^{-1}$)

When the channel cross section is not circular the equivalent diameter of a channel, d_e, is used. For a rectangular cross section of height a and width b, de is given as:

$$de = \frac{2ab}{a+b} \tag{8.2}$$

and the linear flow rate, u, is given by

$$u = \frac{volumetric \quad flow\ rate}{channel \quad area} = \frac{Q}{abl_n} = \left(\frac{m^3/s}{m^2}\right) \tag{8.3}$$

With l_n, the number of channels.

So, for an insert with 7 channels of height 1mm and width 7 mm:

$$de = \frac{2x0.001x0.007}{0.001+0.007} = 1.75x10^{-3}m$$

Using a flow rate of 6 L/m

$$u = \frac{6/(60x1000)}{0.001x0.007x7} = 2.04\ ms^{-1}$$

with 0.5 wt% NaOH solution at 60°C, where $\rho = 987.66\ kgm^{-3}$ and $\mu = 4.54 \times 10^{-4} kgm^{-1}s^{-1}$

$$Re = \frac{1.75x10^{-3} x\ 2.04\ x\ 987.66}{4.54x10^{-4}} = 10332$$

Through rectangular channels the flow follows the following pattern, *Gnielinski* 1994:

< 2300 laminar

2300 < Re < 10000 transition zone

10000 < turbulent

8.4 Solution property measurement (Density and Viscosity)

Solution densities were measured using a 25 ml pyknometer in accordance with BS 733 (1987). The precise capacity of the bottle was calculated at 20°C using a constant temperature water bath (+/- 0.5°C) and RO water. The mass of the bottle and solution was determined using a *Sartorius* balance, accurate to +/- 1 mg. Each solution was left to equilibrate in the water bath for 1 hour. The densities for water, 0.5 wt% sodium hydroxide and Ultrasil 11 solution were determined at 22°C, 30°C, 40°C, 60°C, 80°C.

Table 8.5: Densities of 0.5wt% NaOH solutions at different temperatures [+/- 0.001]

Temperature In °C	Mass of filled pyknometer in g	Mass of NaOH solution in g	Densities in g/L[kg/m³]
22	42.594	25.276	1002.271
30	42.543	25.225	1000.257
40	42.467	25.149	997.2434
60	42.225	24.907	987.6553
80	41.962	24.644	977.2186

Table 8.6: Densities of 0.5wt% Ultrasil 11 solutions at different temperatures [+/- 0.001]

Temperature In °C	Mass of filled pyknometer in g	Mass of Ultrasil 11 solution in g	Densities in g/L[kg/m³]
22	42.563	25.246	1001.062
30	42.513	25.196	999.079
40	42.425	25.108	995.594
60	42.197	24.879	986.533
80	41.901	24.583	974.803

The viscosity of water, VHV-S solution and 0.5 wt% sodium hydroxide and Ultrasil 11 solution were determined at 22°C, 30°C, 40°C, 60°C, 80°C in accordance with BS 188 (1977). A class capillary U-tube viscometer (*Fison Scientific Equipment*) was used for direct flow measurements. The viscometer and the solutions were submerged in a constant temperature water bath (+/- 0.5°C) and the time taken for a determined volume of liquid to flow through a glass capillary was measured. The kinematic viscosity was calculated from the mean of two flow measurements using the following formula:

$$\eta\ (mm^2 s^{-1}) = t \times C \qquad (8.4)$$

t is the time the solution needs to pass from the top mark to the bottom calibration mark and C is constant depending on the type of capillary U-tube viscometer used. With the densities and kinematic viscosities the final dynamic viscosity can be calculated:

$$\mu\ (kgms^{-1}) = \rho(kgm^{-3}) \times \frac{\eta(mm^2 s^{-1})}{10^6} \qquad (8.5)$$

Table 8.7: Kinematic and dynamic viscosities of 0.5wt% NaOH solutions at different temperatures [+/- 0.001]

Temp. in °C	Duration in sec. No.	Duration in sec. No.	Average	Densities in [kg/m³]	Kinematic Viscosities	Dynamic Viscosities
	1	2			$mm^2/s * 10^{-3}$	$kg/ms*10^{-3}$
22	24.25	24.4	1459.5	1002.271	925.450	0.928
30	20.4	20.34	1222.2	1000.257	774.981	0.775
40	17.07	17.03	1023	997.243	648.671	0.647
60	12.06	12.12	725.4	987.655	459.966	0.454
80	9.23	9.2	552.9	977.219	350.586	0.343

Table 8.8: Kinematic and dynamic viscosities of 0.5wt% Ultrasil 11 solutions at different temperatures[+/- 0.001]

Temp. in °C	Duration in sec. No.	Duration in sec. No.	Average	Densities in g/L[kg/m³]	Kinematic Viscosities	Dynamic Viscosities
	1	2			$mm^2/s* 10^{-3}$	$kg/ms* 10^{-3}$
22	25.11	25.05	1504.8	1001.062	954.174	0.955
30	20.4	20.45	1225.5	999.0794	777.074	0.776
40	17.1	16.56	1009.8	995.594	640.301	0.638
60	12.23	12.11	730.2	986.533	463.010	0.457
80	9.25	9.16	552.3	974.804	350.206	0.341

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THE INFLUENCE OF MULTIPLE FOULING AND CLEANING CYCLES UPON THE MEMBRANE PROCESSING OF LIGNOSULPHONATES

A. WEIS and M. R. BIRD

Department of Chemical Engineering, University of Bath, UK

Although the application of pressure-driven membrane technology continues to grow, fouling remains a major unsolved problem. Despite the success achieved with mechanical cleaning methods such as backflushing and backshocking, chemical cleaning-in-place remains the major way to tackle fouling[1–3]. This paper investigates the relationship between fouling and cleaning processes, and how they influence each other over a number of operational cycles. Results are reported for the ultrafiltration of lignosulphonates, which simulates a real industrial filtration problem in the pulp and paper industry. Cleaning was undertaken with both an acid and a commercial aqueous cleaning formulation. Results are presented which show that cleaning performance is strongly dependent upon the nature of the foulant. Results also illustrate the importance of examining membrane performance over several fouling and cleaning cycles.

Keywords: ultrafiltration; vanillin; lignosulphonates; fouling; cleaning.

INTRODUCTION

Lignosulphonates are used as industrial detergents, dispersants, binders and adhesives, finding particular application in the production of animal feeds. Pure fractions of lignosulphonates are necessary for the production of vanillin[4–6].

Separation processes with porous membranes (ultra (UF), micro (MF) and nanofiltration (NF)) are well established industrially and can offer substantial benefits over conventional separation technology. However, membrane fouling often leads to a reduction in permeate flux, and necessitates regular cleaning. Therefore, along with the development of membranes, a substantial amount of research effort has been concentrated on addressing the problem of membrane fouling. Historically, this research was either focused on the parameters which influence fouling, or those which influence cleaning. The objectives were usually to reduce fouling or to improve cleaning. A disadvantage of this method of research was that fouling and cleaning processes were investigated separately, with no consideration given to the fact that the processes are intimately interrelated over a number of operational cycles.

This paper reports work in progress which investigates the efficacy of two cleaning agents in treating membranes over a period of five fouling and cleaning cycles. Permeate flux decline within each cycle was measured, and these measurements were then used to draw conclusions upon the interrelationship between fouling and cleaning processes.

EXPERIMENTAL

The fouling material used was a lignosulphonate product from Borregaard Lignotech, Norway. The product specification can be found in Table 1. During the fouling protocol a product concentration of 0.1 wt% was used. The separation of lignosulphonates from spent sulphite liquor using ultrafiltration membranes mirrors a real separation problem[4–6]. After the sulphite cooking process, wood pulp liquor contains monosaccharides, oligo- and polysaccharides, degraded lignin (called lignosulphonates) and salts resulting from the cooking ingredients. The aim of the UF separation process is to separate lignosulphonate from the sugars and salts to yield a high molecular weight fraction of lignosulphonates in the retentate. The high molecular weight fraction can be used to produce vanillin. Severe fouling occurs during this membrane separation process.

Previous researchers report that lignosulphonates are a major contributary factor in the fouling occuring during the filtration of spent sulphite liquor[7,8]. Therefore, the chemical and steric features of lignosulphonates will intimately affect their fouling performance.

The cleaning cycles were carried out with a widely used formulated cleaning agent, *P3 Ultrasil 11* (0.1 wt%, pH 11.8–12) (Henkel Ecolab), and with nitric acid (0.1 vol.%, pH = 2) (supplied by Fisher Scientific).

P3 Ultrasil 11 is a powder consisting of sodium hydroxide (>40 wt%), EDTA (>30 wt%), anionic surfactants (5 wt%), non-ionic surfactants (5 wt%).

Table 1. Fouling material specification.

Moisture wt%	Dry matter wt%	Ash wt%	Calcium $mg\,kg^{-1}$	Sulfonate group $mmol^{-1}\,kg^{-1}$	Carboxylic group $mmol^{-1}\,kg^{-1}$	Total $mmol^{-1}\,kg^{-1}$
6.6	93.4	9.6	31.4	179	232	411

The membrane used was a Polyethersulphone (PES) ultrafiltration flat-sheet membrane with a molecular weight cut off of 30 kD and an effective membrane area of 95 cm^2 (Hoechst Celgard).

The literature reports that chemical cleaning of membranes is often best at low transmembrane pressures (TMP), high cross-flow velocities (CFV) and moderate temperatures[1–3]. A schematic diagram of the fouling rig is shown in Figure 1. The following experimental protocol was developed:

(i) *Fouling step*: carried out under the following conditions: lignosulphonate solution at a temperature of 20°C, CFV 2.7 ms^{-1}, TMP of 4.2 bar, and a run time of one hour. These conditions gave a decline in permeate flux to a steady value. During fouling CFV, TMP were kept constant and adjusted manually by needle-valves sited before and after the module (see Figure 1). The temperature of the feed was kept constant by the use of a cooling coil situated inside the tanks. During operation the permeate flux was measured every five minutes. After the fouling step, the remaining fouling solution in the pipes and hoses was displaced by reverse osmosis (RO) water to ensure that no lignosulphonates remained in the system.

(ii) A ten minute *rinsing step* with RO water at 20°C, a CFV of 2.7 ms^{-1}, and one bar TMP followed. The permeate line was kept closed. The turbulent flow conditions used (Reynolds number = 4700) created sufficient wall shear stress to wash away any loose material on the membrane surface. After the rinsing step, the pipes and hoses were drained to ensure that no remaining RO water would dilute the cleaning solution used in step (iii).

(iii) The *cleaning step* was carried out under the following conditions: 0.1 vol% nitric acid or 0.1 wt% *Ultrasil 11*, a temperature of 50°C, a CFV of 2.7 ms^{-1}, 1.0 bar TMP, and a run time of 30 minutes. Any cleaning solution remaining in the pipes and hoses was flushed out using RO water.

(iv) An *additional rinsing step* using RO water was carried out, with the permeate line open in order to remove the cleaning agent residing within the membrane structure. A CFV of 2.7 ms^{-1}, a temperature of 20°C, one bar TMP and a run time of 10 minutes were employed.

Following this protocol, the fouling cycle was recommenced. In common with industrial practice, each step was run under turbulent conditions.

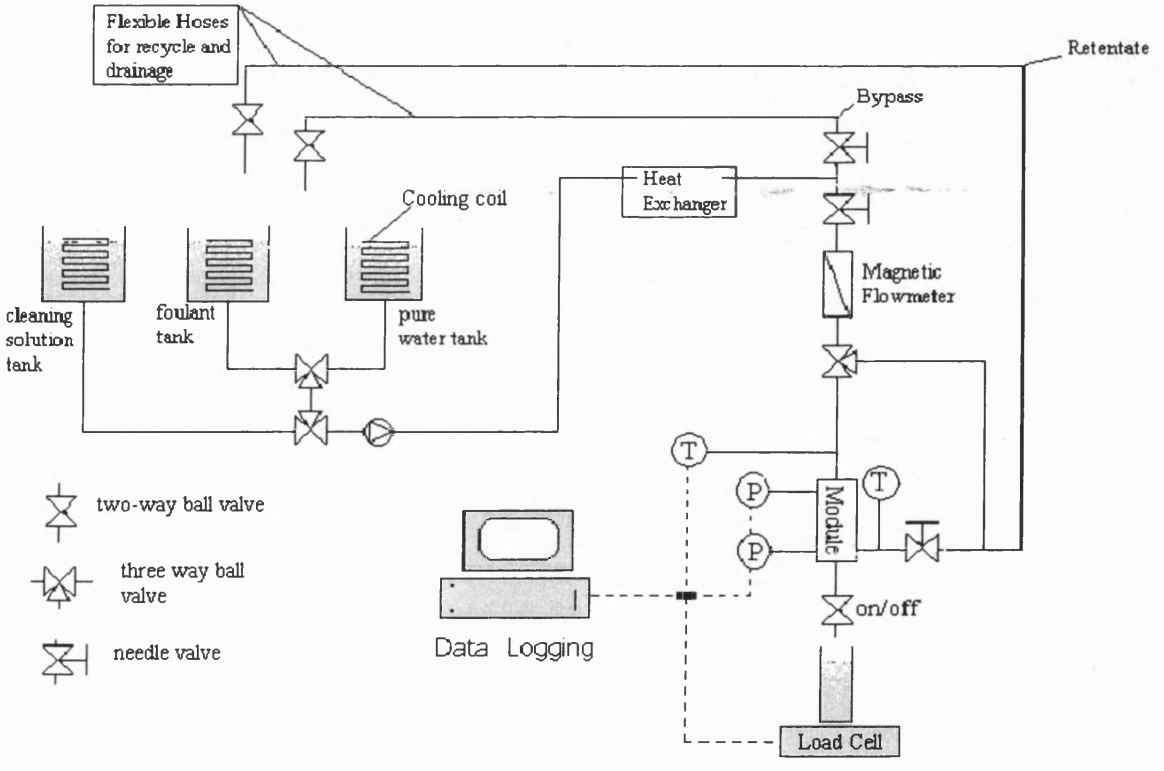

Figure 1. Schematic diagram of the fouling and cleaning rig.

RESULTS AND DISCUSSION

The behaviour of a new membrane during its first filtration cycle is always different to its subsequent performance. For this reason, data from the first operational cycle are not considered to be representative of the membrane's long term performance.

Absolute flux decline values are difficult to compare, because the performance of each of the rectangles of membrane used varied slightly, even though the membranes were cut from the same large sheet. Therefore, in addition to absolute flux decline curves shown in Figure 2, relative values are also presented in Figure 3.

The relative flux decline is calculated from the ratio of (i) the fouling permeate flux, declined to a steady value, and (ii) the initial permeate flux at start of the each fouling cycle (see equation (1)). In each case the initial fouling permeate flux is determined following the previous cleaning cycle.

$$\textit{Relative Flux Decline}\ [\%] = 100 - \frac{J_f}{J_0} \times 100 \qquad (1)$$

where J_0 is the initial fouling flux, and J_f is the final steady fouling flux. The steady fouling flux is achieved when no further permeate flux decline is observed.

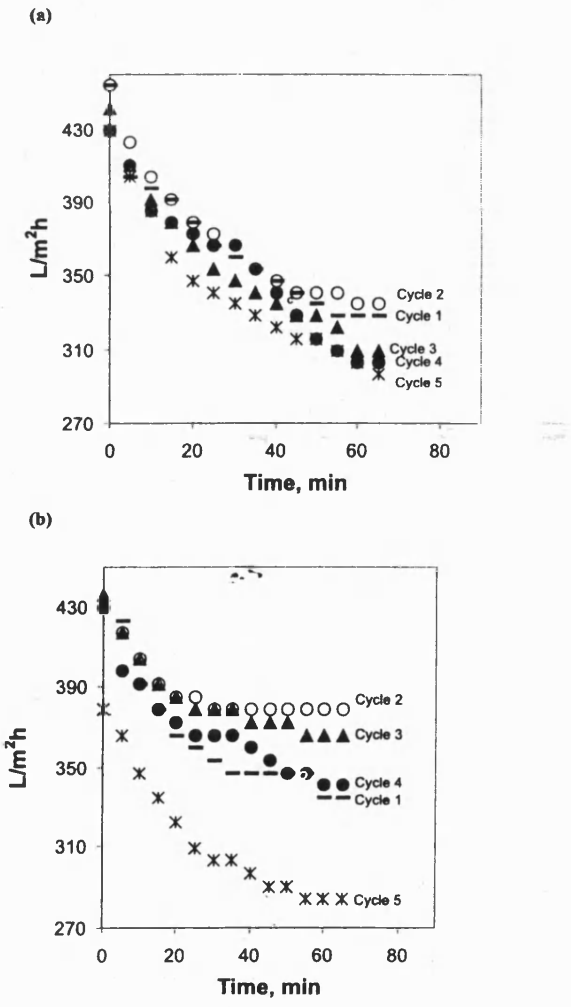

Figure 2. Flux decline curves after a) *Ultrasil 11* b) nitric acid cleaning.

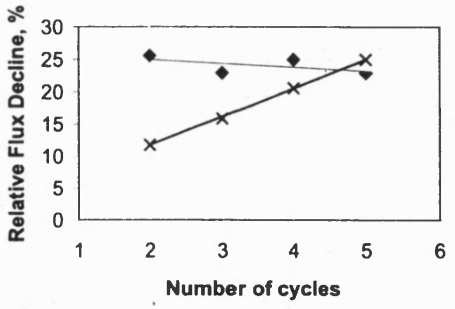

Figure 3. Relative permeate flux decline within each fouling cycle after either *Ultrasil 11* or nitric acid cleaning (◆ *Ultrasil 11*; × Nitric acid).

Figure 3 shows that when *Ultrasil 11* is used, the relative flux decline is almost constant, at approximately 25%. After two cycles of nitric acid cleaning, the initial flux decline is only 10%. However, this flux decline increase by approximately 5% for each subsequent cycle. By the fifth cycle, the relative flux decline when using nitric acid is >25%, larger than the flux decline seen when *Ultrasil 11* is employed.

Ultrasil 11 consists of a cocktail of components, which could display both synergistic or antagonistic behaviour when tackling different cleaning problems. Clearly, an advantage of a formulated cleaner is its generic nature enabling a wide variety of soils to be treated. However, it is unlikely that all components in a formulated cleaning agent are useful or even benign in the treatment of any specific soil.

These results show that there is a significant relationship between fouling and cleaning processes. The fact that over several cycles nitric acid cleaning has a negative effect upon the foulants, probably the lignosulphonates, has lead us to suggest the following hypothesis, which is currently being tested. After each nitric acid clean, the surface probably attracts additional deposition. A possible mechanism for this phenomenon could be the delivery of hydrogen ions to the lignosulphonate anions during cleaning[9]. This would change the overall charge on the membrane, possibly resulting in a higher fouling potential following acid treatment. This behaviour contrasts with that of *Ultrasil 11*, which contains EDTA. This chelating agent would tend to keep cations in solution, and therefore minimize changes to the charge on the membrane surface. Lignosulphonate deposition would therefore maintain its predominantly negative charge, thus repelling additional negatively charged material from adhering to the surface, and reducing the permeate flux.

Surface characterization techniques are currently being employed to test this hypothesis, and to examine the synergy between fouling and cleaning processes over a larger number of operational cycles.

CONCLUSIONS

These results demonstrate the importance of examining the effectiveness of cleaning agents over a large number of operating cycles, rather than relying upon data obtained from a single fouling and cleaning operation. Over a small number of fouling and cleaning cycles, the performance of nitric acid is superior to that of *Ultrasil 11*. However, after 5 cycles, it is clear that this position is reversed, with *Ultrasil*

11 appearing to be the more effective of the two cleaning agents.

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ADDRESS

Correspondance concerning this paper should be addressed to Dr M. R. Bird, Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail M.R.Bird@bath.ac.uk

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The chemical cleaning of polymeric UF membranes fouled with spent sulphite liquor over multiple operational cycles

Andreas Weis [a], Michael R. Bird [a,*], Marianne Nyström [b]

[a] *Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, UK*
[b] *Department of Chemical Technology, Centre for Separation Technology (CST), Lappeenranta University of Technology, P.O. Box 20, Lappeenranta 53851, Finland*

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Abstract

Whilst permeate flux is an important parameter in characterising synthetic membrane performance, it is a poor indicator of surface condition. Membrane pores may be fouled, but the charge of the fouled surface is critical in determining performance. Polyethersulphone (PES) and polysulphone (PSf) ultrafiltration membranes were fouled with spent sulphite liquor and cleaned using sodium hydroxide and Ultrasil 11 over several operating cycles. The Osmonics PSf membrane displayed a greater relative flux decline over several cycles than the Nadir PES membrane. After 15 fouling and cleaning cycles, the relative flux decline for the PSf membrane was 70% and 55% when cleaning with NaOH and Ultrasil 11, respectively. The corresponding relative flux decline figures for the PES membrane after 15 cycles were 45 and 30% for NaOH and Ultrasil 11 cleaning, respectively. Performance and zeta-potential graphs are presented that demonstrate the strong relationship between the fouling and cleaning history, the surface charge and the performance of the membranes in terms of flux recovery.

Keywords: Ultrafiltration; Lignosulphonates; Fouling; Cleaning; Zeta-potential

1. Introduction

Along with the development of membranes, a substantial amount of research effort has been concentrated on addressing the problem of membrane fouling. Historically, this research was either focused on the parameters that influence fouling, or those that influence cleaning. However, both steps are ultimately likely to be interrelated.

A cleaning agent can affect fouling material present on a membrane surface in three ways: (i) the foulants may be removed, (ii) the morphology of the foulants may be changed (e.g. by swelling or compaction [1,2] or (iii) the surface chemistry of the deposit may be altered so that the hydrophobicity or charge is modified. Changes in surface charge can be determined by the use of zeta-potential measurements [3].

The use of an inappropriate cleaning agent could adversely affect performance in one or more of the above categories. In this study, the interaction of foulant and cleaning agents is considered over several operational cycles.

An experimental system was developed for the ultrafiltration of spent sulphite liquor, for the separation and concentration of high molar mass lignosulphonates [4]. This separation is well established in industry, but fouling still remains a problem.

The sulphite liquor is a by-product of the chemical pulp production and contains mainly: (i) sulphonated

* Corresponding author.
E-mail address: m.r.bird@bath.ac.uk (M.R. Bird).

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lignin (called lignosulphonates), (ii) cooking chemicals (such as calcium sulphate) and (iii) various sugars (such as pentose). The phenolic compounds are thought to contribute most to the fouling problem during the lignosulphonate separation. This separation process was selected for study, as the phenolic compounds present are relatively well understood. Phenols, like humic acids, are also important foulants in water purification.

Earlier work in our laboratory [4] suggested that the organics present are able to react with metal-ions, like Ca^{2+} or Na^{+}, to form complexes. Lignosulphonates are thought to form spherical structures under acidic, neutral and alkaline conditions, with charges on the surface. Kontturi [5,6] determined the effective degree of dissociation of the two functional groups, with an increase towards alkaline environments. At pH 11, 80% of all functional groups in lignosulphonates are dissociated. If cleaning is carried out with NaOH or Ultrasil 11, a favourable alkaline environment is created, and interaction could take place for instance with monovalent ions in the following manner:

$$R\text{–}COO^{-}H^{+} + NaOH \rightarrow R\text{–}COO^{-}Na^{+} + H_2O \quad (1)$$

This ion exchange would reduce the pH from alkaline towards neutrality. In practice this pH-change can be measured clearly when cleaning with NaOH. In addition, monovalent cations can be preferentially displaced in favour of divalent cations such as calcium. These interactions lead to a complex chemistry, but it seems likely that the ethylene diamine tetra acetic acid (EDTA) sequesterant present in Ultrasil 11 is complexing with Ca^{2+}, and consequently no cations remain to complex with phenolic compounds in the fouling material, thereby improving cleaning. If NaOH is used alone, then no protective effect of EDTA is present, and this should result in a poorer cleaning performance.

2. Experimental materials and methods

2.1. Foulants

The fouling material used was spent sulphite liquor supplied by Borregaard Lignotech Ltd. (Norway). The product specification is shown in Table 1. The separation of lignosulphonates from spent sulphite liquor using ultrafiltration membranes mirrors a real separation problem [7–9].

Table 1
Lignosulphonate specification

Product	Amount
Moisture (%)	85.4
Dry matter (%)	14.6
Ash (%)	10.2
Calcium (mg kg^{-1})[a]	24.88
Sulfonate group (mmol kg^{-1})[a]	107
Carboxylic group (mmol kg^{-1})[a]	125
Total (mmol kg^{-1})[a]	232

[a] Calculated on a dry weight basis.

After the industrial sulphite cooking process, wood pulp liquor contains monosaccharides, oligo- and polysaccharides, degraded lignin (called lignosulphonates) and salts resulting from the cooking ingredients. The aim of the UF separation process is to separate lignosulphonate from the sugars and salts to gain a high molar mass fraction of the lignosulphonates in the retentate. The high molar mass fraction can be used to produce vanillin. During the membrane separation process severe fouling occurs. Previous researchers report that lignosulphonates are a major contributory factor in the fouling occurring during the filtration of spent sulphite liquor [10,11]. Therefore, the chemical and steric features of lignosulphonates will intimately affect their fouling performance.

2.2. Cleaning agents

The cleaning cycles were carried out with a widely used formulated cleaning agent, P3 Ultrasil 11 (Henkel Ecolab), and with sodium hydroxide (Fisher Scientific). P3 Ultrasil 11 consists of sodium hydroxide (ca. 44 wt.%), tetra sodium salt of EDTA (>30 wt.%), anionic surfactants (<5 wt.%), non-ionic surfactants (<5 wt.%).

2.3. Membranes

The membranes used were polyethersulphone (PES, Nadir Filtration) and polysulphone (PSf, Osmonics) ultrafiltration flat-sheet membranes with a cut off of 30 ku (30 kDa) and an effective membrane area of 95 cm^2.

2.4. Method

The following protocol was developed:

1. *Conditioning*: the membranes were treated for 15 min at 22 °C with 0.1 wt.% Ultrasil 11:
   - Nadir: trans-membrane pressure (TMP) of 150,000 Pa (1.5 bar), a cross flow velocity (CFV) of 1.8 m s^{-1}, permeate valve open.
   - Osmonics: TMP 10^5 Pa (1.0 bar), CFV 1.8 m s^{-1}, permeate valve open.

   The system was drained and rinsed with RO water.
2. *Pure water flux measurements*: measured once the flux was steady under the following conditions:
   - Nadir: TMP 525,000 Pa (5.25 bar), CFV 2.7 m s^{-1}, open permeate valve.
   - Osmonics: TMP 525,000 Pa (5.25 bar), CFV 2.7 m s^{-1}, open permeate valve.

   The system was drained
3. *Fouling*: a fouling time of 90 min at 70 °C was found most suitable and similar to industrial separation:
   - Nadir: TMP 825,000 Pa (8.25 bar), CFV 2.7 m s^{-1}, open permeate valve.
   - Osmonics: TMP 700,000 Pa (7.00 bar), CFV 2.7 m s^{-1}, open permeate valve.

   The system was drained and rinsed with RO water.
4. *Rinsing*: to remove lose deposits on the membrane surface the system was rinsed for 15 min at 22 °C:
   - Nadir: TMP 150,000 Pa (1.5 bar), CFV 1.8 m s^{-1}, open permeate valve.
   - Osmonics: TMP 10^5 Pa (1 bar), CFV 1.8 m s^{-1}, open permeate valve.

   The system was drained and rinsed with RO water.
5. *Cleaning*: duration was 30 min, with 0.5 wt.% NaOH or Ultrasil 11 at 22 °C:
   - Nadir: TMP 150,000 Pa (1.5 bar), CFV 1.8 m s^{-1}, open permeate valve.
   - Osmonics: TMP 10^5 Pa (1.0 bar), CFV 1.8 m s^{-1}, open permeate valve.

   The system was drained and rinsed with RO water.
6. *Pure water flux measurements*: measured under the following conditions after a stable flux value was reached:
   - Nadir: TMP 525,000 Pa (5.25 bar), CFV 2.7 m s^{-1}, open permeate valve.
   - Osmonics: TMP 525,000 Pa (5.25 bar), CFV 2.7 m s^{-1}, open permeate valve.

The system was drained and a new fouling cycle can follow.

Product (fouling) flux values were used to assess the efficiency of the cleaning process, as they are usually more meaningful than pure water flux values. The quality of the performance of each cycle was established as follows:

$$\text{flux decline} = 1 - \frac{J_n}{J_0} \tag{2}$$

where J_n is the final (steady-state) flux of the nth ultrafiltration cycle after the rinsing–cleaning–rinsing step, and J_0 is the flux of the virgin, unfouled membrane.

2.5. Determination of foulants precipitated on the membrane

The identification of foulants was done either by extraction of organics or by ATR–FTIR analysis of the deposits at the surface and in the substructure.

The advantage of organic extraction is in quantifying the exact amount of the different precipitated organics present. FTIR is a good way of confirming the result of the extraction work, and gives a detailed screen of the molecular functional groups involved in fouling. In addition, the membrane's polymeric nature can be evaluated, and possible manufacturer modifications made to the polymer can be revealed.

2.6. Organic extractives precipitated on the membrane

The extraction of organics from the fouled membranes was carried out using a method developed by Puro et al. [12]. The principal of the method is that fouled membrane pieces are treated with a solvent in a soxhlet extraction apparatus, to facilitate the removal of organic foulants from the membrane. The extract is then freeze-dried and prepared for analysis of the different organic components in the gas chromatograph. The type of solvent also determines the quantity of

the organic foulants detected, since every solvent has different extraction properties. Puro et al. [12] investigated several extraction procedures with different solvents, and found a 9:1 ratio of acetone:water to be the most suitable.

2.7. FTIR

A Perkin-Elmer 2000 FTIR apparatus was used in this study. This equipment was provided with a HeNe laser as a radiation source (unpolarized IR radiation), tryglycerine sulphate (TGS) as a detector and optical KBr as a beam splitter. The resolution of the FTIR apparatus was adjusted to $2.0\,cm^{-1}$, the optical path difference (OPD) velocity to $0.2\,cm^{-1}$ and the data collecting interval to 1.0. A KRS-5 crystal (thallium bromide iodide) was used as an internal reflection element (45°, 17 reflections). Every spectrum was made of 100 co-added scans [12]. All membrane specimens investigated were dried for 24 h at room temperature prior to use. The spectral positions of different structures are shown in Table 3.

2.8. Zeta-potential measurements

The surface charge on a synthetic membrane has a significant influence on its separation properties and fouling tendencies. The surface charge density of a porous membrane is related to the zeta-potential of the membrane. A theoretical explanation of the surface effects of streaming and zeta-potential can be found in Nyström et al. [3].

Measurements were carried out using a flat-sheet ultrafiltration module equipped with two sets of Ag/AgCl electrodes, that could measure the streaming potential developed across the membrane (zeta-potential in the pores). A membrane with an area of $4.6\,cm^2$ was inserted into the module, compacted and stabilised at a constant pressure and flow rate. The streaming potential measurements were performed with $10^{-3}\,mol\,dm^{-3}$ (10^{-3} M) KCl solution. The first series of measurements were made at a pH of 5.7, that of the KCl solution. The pH range 4–7 was covered. Below pH 3, the great conductivity that developed disturbed the measurements. At pH values above 7, the electrodes were damaged. The flux was measured simultaneously with the streaming potential–pressure curves.

With the streaming potential, the zeta-potential (ζ) can be calculated with the help of the Helmholtz–Smoluchowski equation [16]:

$$\zeta = \frac{\Delta E}{\Delta p}\frac{\eta\kappa}{\varepsilon_0\varepsilon_r} \tag{3}$$

where ΔE is the streaming potential, Δp the transmembrane pressure drop, η the viscosity of the solvent, κ the conductivity of the electrolyte in the pores (approximated as bulk conductivity), ε_0 the permittivity of a vacuum, and ε_r the relative dielectric constant of the electrolyte.

In calculating zeta-potentials (ζ) from streaming potential versus pressure ($\Delta E/\Delta p$) measurements, the Helmholtz–Smoluchowski equation was used without corrections.

3. Experimental results and discussion

3.1. Organic extraction—results

The extraction of organics from the fouled membranes was carried out using a method developed by Puro et al. [12]. The results are displayed in Tables 2 and 3.

The main foulants present on both membranes were fatty acids, resin acids and lignans. In wood pulp in general, about 25% of the total amount of lipophilic extractives at pH 5 are fatty and resin acids. About 5% of these are dissolved in the pulp, and only this dissolved fraction can be found on the membrane. The total amount of extractives found on the PES membrane exceeds that detected on the PS membrane ($38.6\,mg\,m^{-2}$ versus $24.4\,mg\,m^{-2}$, respectively).

Table 2
Organic extractives for 15× fouled and NaOH cleaned PSf and PES membranes

	PS (Osmonics; $mg\,m^{-2}$)	PES (Nadir; $mg\,m^{-2}$)
Fatty acids	9.1	17.7
Resin acids	9.6	17.9
Lignans	13.8	15.6
Sterols	1.9	2.0
Steryl esters	2.3	1.0
Triglycerides	1.5	0.0
Lipophilic extractives (without lignans)	24.4	38.6

Table 3
Possible structures found by the Perkin-Elmer search program

Class number	PSU	Possible bands (cm^{-1})
201	Alkyl-group-general	3330, 2860, 1490, 1235, 1150, 1100, 1070
259	Aromatic compound	1580, 1490, 1320, 1290, 1240, 720, 700
267	Aromatic compound, 1,4-substituted	1495, 830
402	Hydroxy-group	3330, 1235, 1150, 1100, 1070
511	Aliphatic alcohol	3330, 2940, 1490, 1010
2710	Aryl-ether	1580, 1490, 1295, 1150, 1100
2724	Phenoxy-general	1580, 1490, 1295, 1235, 1150, 1100, 1070, 870, 830, 720, 700
2906	Aromatic primary amine	1580, 1490, 1295
4002	Aromatic sulphone	1580, 1490, 1320, 1290, 1150, 1100, 1070, 870, 830, 720, 700

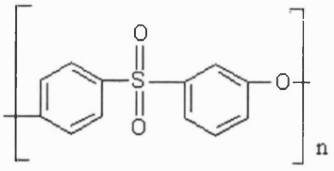
3.2. FTIR results—virgin membranes

The structure of Udel and Victrex polysulphone membranes is shown in Fig. 1, along with the FTIR peaks in the spectra. Fig. 2 shows the FTIR spectra of virgin PES and PSf polymers. The three large peaks at 3330, 2850 and 1650 cm^{-1} represent either aliphatic alcohols, or ether alcohols [13]. The peaks represent primary, secondary, tertiary and cyclic alcohols, and probably come from the manufacturer's commercial preservation agent, glycerine. The peaks between a wavelength of 1700–500 cm^{-1} are typical of those for a polymer made of Udel polysulphone (see Fig. 1).

Very similar FTIR spectra are reported in the literature for membranes made of Udel polysulphone polymer [14,15]. The only peak in that range that is unusual for polysulphone occurs at 1040 cm^{-1}. The search program indicates that this peak comes from an aliphatic alcohol; probably glycerine.

The intensity of peaks for the Osmonics polysulphone membrane is much greater than for the Nadir polyethersulphone membrane, (Fig. 2, for wavelengths less than 1500 cm^{-1}). The Osmonics polysulphone membrane displays a peak at 1065 cm^{-1} that is missing for the Nadir membrane. The search program indicates that this peak represents alkyl groups, such as methyl in Udel polysulphone. Since this peak is missing for the Nadir membrane, it can be concluded that this membrane is composed of Victrex polyethersulphone.

Udel polysulphone



Victrex
polyethersulphone

Fig. 1. Chemical structures of different membrane polymers.

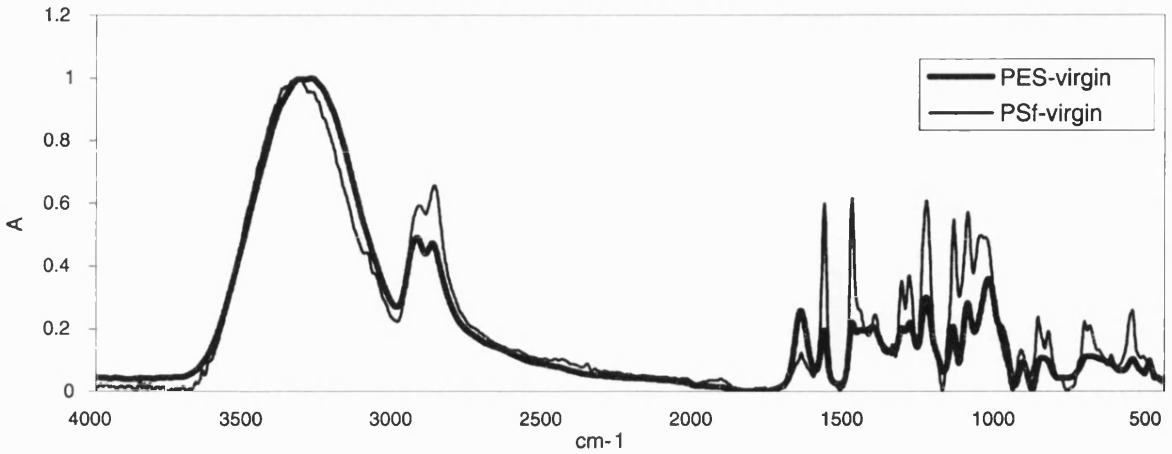


Fig. 2. FTIR spectra of the virgin polyethersulphone (Nadir) and polysulphone (Osmonics) membrane. ATR-method, 45° incident angle, KRS-5 crystal, resolution 2.0 cm^{-1}.

3.3. FTIR results—membranes fouled once

Fig. 3 shows that for the PSf membranes fouled once, peaks at 3330, 2850 and 1650 cm^{-1} have almost disappeared, but the peak at 2850 cm^{-1} for the PES membrane is only reduced in intensity. However, the PES membrane peak at 3330 cm^{-1} is still unchanged from that of the virgin membrane. Between 3600 and 3000 cm^{-1}, the PSf membrane shows a low intensity broad absorption band, with peaks at 3400 and 2950 cm^{-1}. This indicates the start of fouling, since these wavelength areas and peaks are characteristic for lignosulphonates [15]. There are almost no new peaks appearing in either spectrum between 1700 and 500 cm^{-1}, except very small ones at 1520, 1410 and 1010 cm^{-1}, that are also likely to result from lignosulphonates. As they also appear in the spectras for membranes fouled 15 and 21 times (Figs. 4 and 5, respectively), it is likely that they are not simply background noise.

3.4. FTIR results—multiple fouled membranes

No new peaks appear or disappear in the spectra for multiple fouled and cleaned membranes, which have not already been seen for the virgin and once-fouled membranes (Figs. 4 and 5). The important peaks indicating lignosulphonate fouling become more intense, especially for the NaOH cleaned membranes. Surprisingly, the peaks resulting from the membrane

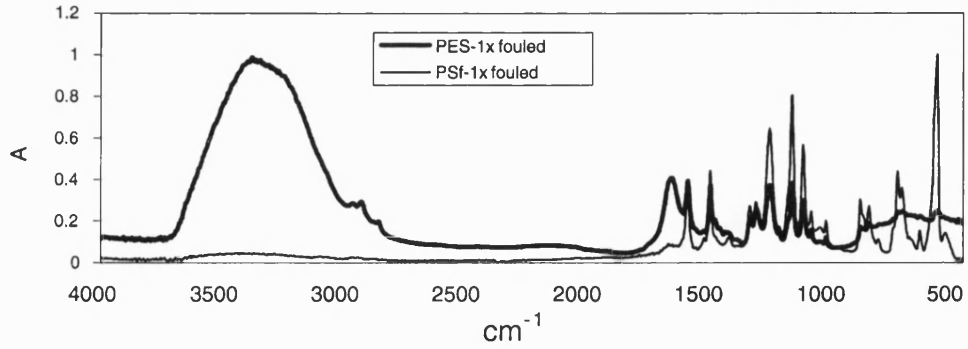


Fig. 3. FTIR spectra of once-fouled polyethersulphone (Nadir) and polysulphone (Osmonics) membrane.

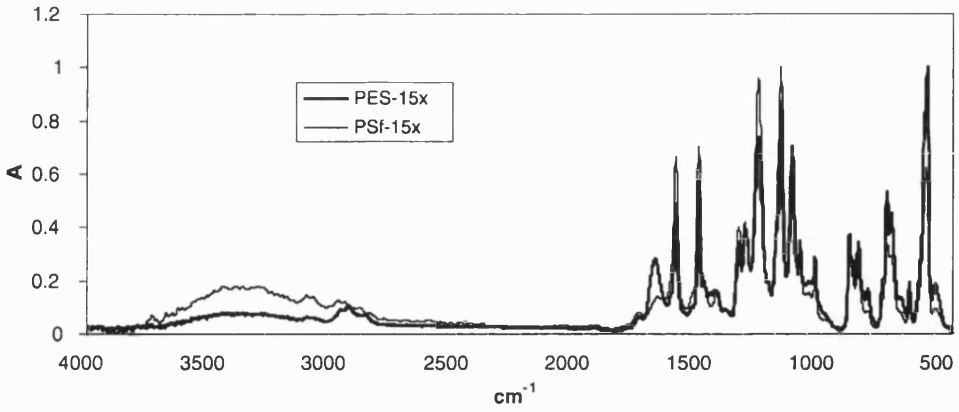


Fig. 4. FTIR spectra of 15× fouled and NaOH cleaned polyethersulphone (Nadir) and polysulphone (Osmonics) membrane.

polymers, between a wavelength of 1750 and 500 cm^{-1} also become more intense. One possible explanation for this observation is that the removal of glycerine (which disturbs measurements) occurs more completely as greater numbers of fouling and cleaning cycles are completed.

3.5. Results for product flux recovery

In Figs. 6 and 7 the relative total flux decline values for the cleaning of a polyethersulphone and polysulphone membrane are shown. Absolute flux decline values are difficult to compare (see Fig. 8), because the performance of each of the rectangles of membrane used varies, even though the membranes were cut from the same large sheet. Relative flux decline values therefore provide a better indication of performance trends.

A progressive decline in performance with increasing cycle number is seen when cleaning with both NaOH and Ultrasil 11, for both polysulphone and polyethersulphone membranes.

The performance of NaOH is as good as that of Ultrasil 11 over the first six operational fouling and cleaning cycles. However, from 6–15 cycles it is clear that Ultrasil 11 is a superior cleaner to NaOH for both PSf and PES membranes, as the rate of increase of flux decline with cycle number is reduced.

An explanation for this behaviour could be the interaction of Ca^{2+} ions with phenolic compounds and acids present in the spent sulphite liquor and subsequently with the deposit on the membrane surface.

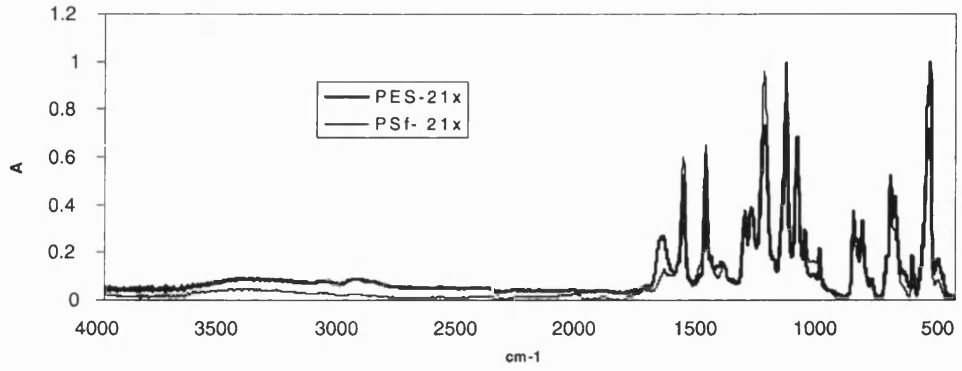


Fig. 5. FTIR spectra of 21× fouled and NaOH cleaned polyethersulphone (Nadir) and polysulphone (Osmonics).

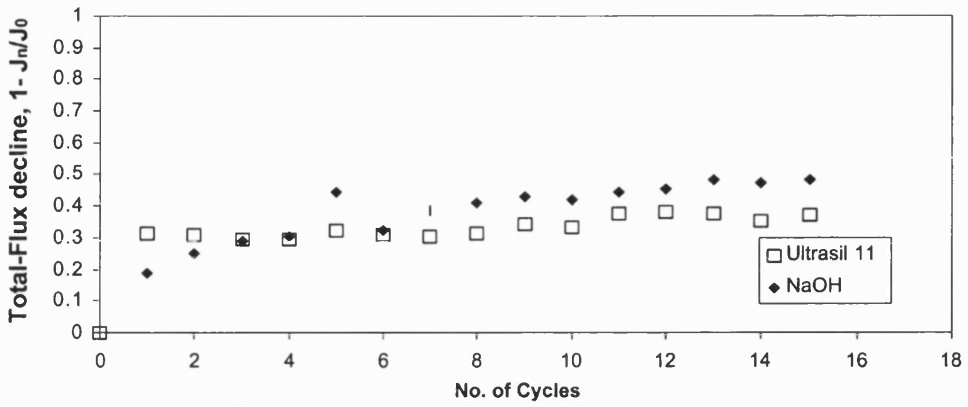


Fig. 6. Comparison of product flux decline values after NaOH and Ultrasil 11 cleaning of a Nadir polyethersulphone membrane.

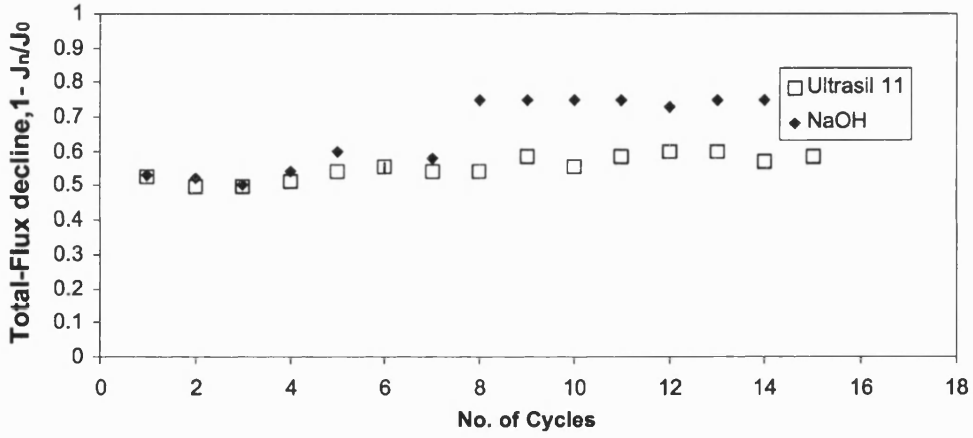


Fig. 7. Comparison of product flux decline values after NaOH and Ultrasil 11 cleaning of an Osmonics polysulphone membrane.

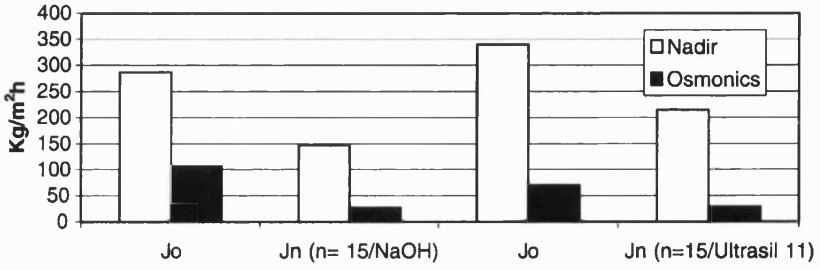


Fig. 8. Product fluxes for two sets of virgin membranes (J_0) to show natural variation (first and third sets of blocks). Also shown are fluxes for each set of membranes after $n = 15$ fouling/cleaning cycles (J_n) using NaOH and Ultrasil 11 cleaning agents (second and fourth sets of blocks, respectively).

Over a single cycle, NaOH might be able to compete with the performance of Ultrasil 11. However, if fouling and cleaning cycles are repeated, the chelating agent EDTA present in Ultrasil 11 will prevent Ca^{2+} from interacting with the phenolic and acidic compounds present [17]. This maintains the negative charge on the membrane surface, and the deposit resists further interaction (fouling) with negatively charged organic groups. This may explain the superior long-term performance of Ultrasil 11.

If Ca or Na ions are reacting with the sulphonate or the carboxyl groups in the lignin, this should be seen in a change of the surface charge, or zeta-potential.

3.6. Results for zeta-potential measurements

In Fig. 9a, the zeta-potentials for virgin and once-fouled membranes can be seen. The values for the virgin PES membrane are fairly constant throughout the tested pH range and kept slightly below zero, which means charge neutrality. The PSf membrane shows a different picture, with a strong declining slope towards alkaline pHs. This observation indicates that the PSf membrane surface is becoming negatively charged as pH increases, due to the adsorption of negatively charged ions. This in turn could attract metal cations, such as calcium, which could attract further anions such as lignosulphonates, if they were present (they are not present in this case).

The once-fouled membranes show an increase in negative charge resulting from the adsorption of lignosulphonates. It becomes clear that the influence of the virgin membrane upon the zeta-potential is negligible, and that the charge results solely from the foulants. This is apparent, as the zeta-potential is constant over the pH range from 3 to 7, which is typical for lignosulphonates. The other main foulants, fatty acids and resin acids have a negligible influence on the zeta-potential. In the case of fatty acids in general, a sharp transformation can be seen from the dissociated into the undissociated form of the acid from neutral towards acidic pH values [18]. The negative head group of the fatty acids would therefore contribute to the zeta-potential only a little at acidic pH values. For the other main foulant, the resin acids, the contribution to the zeta-potential can be seen as absent. For the 11 most common resin acids extracted from wood, the pK_a value is between 5.7 and 6.4 [19]. At pH values below their pK_a, the resin acids are virtually unionized and therefore do not contribute to the measured zeta-potential below 6.4. Both types of acids are major foulants, and are largely responsible for the flux decline appearing during the ultrafiltration. It is also likely that sodium or calcium could still have reacted with the fatty acids or the resin acids, but they will not affect the zeta-potential, since at the measured pH values both types of acids are not dissociated to any great extent.

Furthermore, the fouled PSf membrane has a 2 mV lower charge than the PES membrane, which could indicate a stronger fouling tendency.

Fig. 9b shows that for the PES membrane, the effect of NaOH cleaning is to change the zeta-potential to approximately 4.5 mV, from that of approximately −8 mV seen for the 1× fouled membrane shown in Fig. 9a. The zeta-potential changes from −8 to approximately −7 mV for 1× fouled membrane when Ultrasil 11 cleaning agent is used (Fig. 9b).

These results support the product flux recovery data for the first fouling/cleaning cycle seen in Fig. 6, when NaOH gave a better flux recovery than Ultrasil 11.

For the PSf membrane the reduction in zeta-potential for both cleaning agents is the same, approximately from −10 to −9 after cleaning. This also supports the flux recovery values seen in Fig. 7, since they are also the same for both cleaning agents after a single cycle.

Fig. 9c shows that after multiple fouling and cleaning cycles, the zeta-potentials for the PES membrane are the same as those for the once-fouled membranes shown in Fig. 9a. This is true for both NaOH and Ultrasil 11 cleaning treatments. This observation does still indicates a cleaning effect, since the potential was maintained at −8 mV. However, this value cannot explain the superior performance in flux recovery for Ultrasil 11 in comparison to NaOH over the long-term. The same trend is observed for the PSf membrane subjected to multiple fouling and cleaning cycles (Fig. 9c). The potential is slightly worse than that for a once-fouled membrane, and there is no observable difference for cleaning with either NaOH or Ultrasil 11. As before, this does not explain why the performance of Ultrasil 11 is superior to that of NaOH over the long-term.

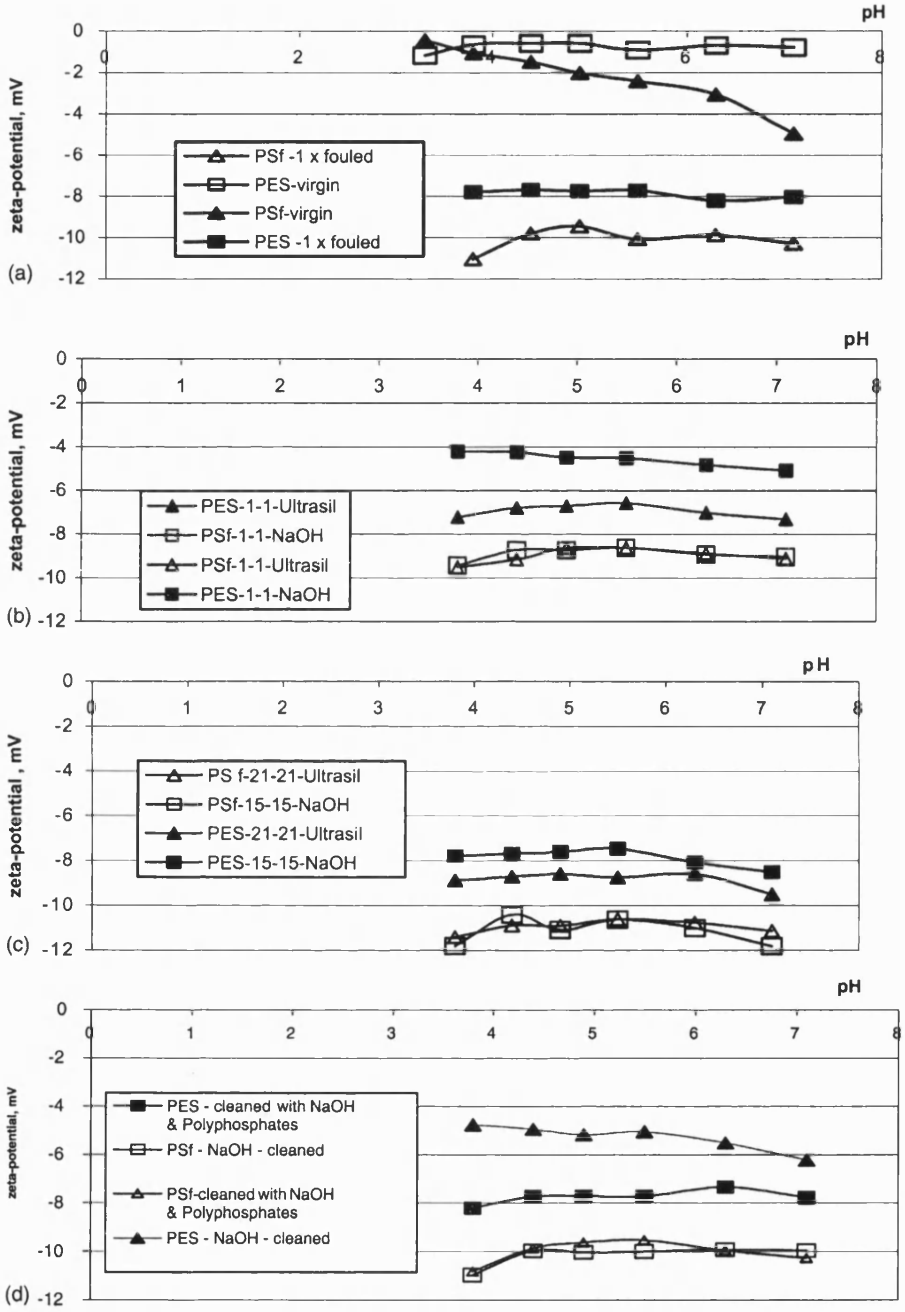


Fig. 9. Zeta-potential at different pH values for polyethersulphone (PES) and polysulphone(PSf) membranes: (a) virgin and once-fouled, (b) once-fouled and once cleaned with either NaOH or Ultrasil 11, (c) subjected to 15 fouling/cleaning cycles and 21 fouling/cleaning cycles, (d) subjected to sequential cleaning with first NaOH and then polyphosphate.

3.7. Zeta-potentials after sequential cleaning

The observed zeta-potential for single and multiple fouled and cleaned membrane could result from: (i) removing or attaching foulants on the membrane surface or pores, or (ii) the neutralizing effects of the metal cations in the cleaning agent. To determine which of these mechanisms was dominant, a single fouled membrane was first treated with NaOH, and then subsequently with polyphosphate, a sequesterant. Fig. 9b showed that cleaning a PES membrane with NaOH alone reduced the zeta-potential by almost a half. The standard deviation in the results for all membrane samples was 0.5 mV. This value was calculated after measuring different fouled and cleaned membrane sheets of different age, stored in pure water. After this treatment, the same membrane was cleaned with polyphosphate (Fig. 9d), using the same parameters as for NaOH cleaning. Any removal of phenolic compounds could clearly be measured using a spectrophotometer (absorbance measured at 280 nm). After cleaning, it was expected that the zeta-potential would rise again and return close to the value of a virgin PES membrane, especially as the pure water flux after the cleaning returned almost to the value of the pristine membrane. Perhaps surprisingly, the zeta-potential value dropped once more to −7.9 mV, a value that is close to that of the once-fouled membrane. This suggest strongly that the removal of foulants does not necessarily lead into the reduction of zeta-potential and must represent other effects, such as the removal of cations by the sequestrant and therefore the observed drop in zeta-potential. For the PSf membrane, no change in zeta-potential could be observed.

The zeta-potentials after different cleaning protocols are applied to the PES membrane and can be compared using normalized zeta-potentials. To calculate the normalized value, the average zeta-potential in mV was first calculated with the values over the measured pH range. This was possible, since the zeta-potential remained stable over the whole pH range without exception. The value of the once-fouled membrane was set at 100%, in order to investigate how the potentials change after a particular protocol is applied. The following equation was used:

$$\psi = \frac{\zeta_n}{\zeta_{1\times f}} \times 100\% \quad (4)$$

where ψ is the normalized zeta-potential in percent, $\zeta_{1\times f}$ is the zeta-potential of the once-fouled membrane and ζ_n is the zeta-potential for membranes subjected to sequential fouling and cleaning protocols.

The normalized zeta-potential values recorded were as follows: once-fouled then once cleaned with NaOH, 58%, once-fouled then once cleaned (NaOH) and once cleaned (polyphosphate), 98.7%, once-fouled and then once cleaned with Ultrasil 11, 88.3%, 15× fouled and each time cleaned with NaOH, 100%, and finally 21× fouled and each time cleaned with Ultrasil 11, 112.6%.

For the PSf membrane, the zeta-potentials do not significantly vary with cleaning treatment.

4. Conclusions

The extraction work and FTIR measurements show that the major foulants are fatty acids, resin acids and lignans. All three contribute to the flux decline during the ultrafiltration and also interact with their functional groups with metal ions, but only the lignan is likely to contribute significantly to the zeta-potential results at different pH values.

The foulants adhere with a hydrophobic portion to the membrane surface, and stretch their negative groups into the solution. This change of potential is quite large for single fouled and NaOH cleaned PES membrane. For Ultrasil 11 cleaned membrane the change is small and it looks as if the EDTA leaves the functional groups of the lignosulphonates in a pristine state.

For the PSf membrane, hardly any change in zeta-potential can be observed when using different cleaning agents. This indicates that the first cycle is already decisive in determining future performance. Over the long-term, there is no significant change in zeta-potential observed, no matter what cleaning agent is used. This indicates that charge effects do not play an important role for the flux recovery over multiple cycles.

Changes in zeta-potential seem to be a function of the interaction between the lignosulphonate and metal cations. The sequestrants play a major role in this interaction. The charge of the virgin membrane, the morphology and most importantly the hydrophilicity, all appear to influence the foulant–cleaner interaction.

The hydrophilicity will be the subject of further investigation.

Overall, the Osmonics polysulphone membrane displayed a greater relative flux decline over several cycles than the Nadir polyethersulphone membrane. After 15 fouling and cleaning cycles, the relative flux decline for the polysulphone membrane was 70% and 55% when cleaning with NaOH and Ultrasil 11, respectively. The corresponding relative flux decline figures for the polyethersulphone membrane after 15 cycles were 45 and 30% for NaOH and Ultrasil 11 cleaning, respectively.

The performance of Ultrasil 11 is better than NaOH over long-term (greater than six fouling and cleaning cycles). Over short term, the picture is somewhat different. For PES, cleaning with NaOH gives at least as good results as Ultrasil 11. For PSf, NaOH performs as well as Ultrasil 11 up to the seventh cycle, after which time Ultrasil 11 is clearly better.

The zeta-potential is a very important tool in determining the quality of cleaning. The sequential cleaning experiment clearly showed that a change in zeta-potential is not solely dependent upon the removal or attachment of foulants to the membrane surface. Rather, the zeta-potential change is entirely due to foulant–cleaner interaction. The influence of zeta-potential appears to be as important as deposit removal in determining permeate flux. Separation of the relative contributions of zeta-potential and deposit removal upon flux recovery will be subject of future studies.

For PES membrane, the reduction or maintaining of zeta-potentials due to cleaning leads to a phenomenon called modified self-rejection [20], a phenomenon similar to the attachment of anionic surfactants on the membrane surface repelling other anionic molecules. The more negative zeta-potential following Ultrasil 11 cleaning leads to a more stable long-term performance due to the repulsion of other negatively charged molecules. PES membranes cleaned with NaOH display a less negative zeta-potential, and lack the ability to repulse, and the drop in performance therefore continues with increasing fouling/cleaning cycles.

Over the short term, the membrane material, its porosity, and surface roughness, are probably the dominant factors in determining the cleaning performance. Over the long-term, the surface becomes irreversibly fouled, and the physico-chemical interactions between cleaning agent and foulant are dominant, and the influence of the membrane material itself becomes less significant.

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